Ultrasonically assisted preparation of polyurethanes and polylactones

Lenz, Emma

Award date:
1995

Awarding institution:
University of Bath

Ultrasonically Assisted Preparation of Polyurethanes and Polylactones

Submitted by Emma LENZ
for the degree of PhD
at the University of Bath

1995

Emma Lenz

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Acknowledgements

Above all, my thanks goes to Dr. Gareth Price for his ideas, enthusiasm and good humour throughout my three years work. I appreciate the time he has always made to help me and in particular his uncanny knack for making a completely dead instrument spring into life by his very presence.

I am very grateful to Dr. Chris Ansell of Smith and Nephew Ltd. for the arrangement of a CASE Award to support my studies and for always being ready to offer advice and help. I particularly value the time I was able to spend working at Group Research in Harlow and York.

Back at Bath, Adam and Liz gave me much needed technical support and clean glassware and I'd especially like to thank Joe Stainer for always managing to find the equipment I needed and for mending everything I broke!
To my fellow students: Steve, Simon and Andy - thanks for creating a lively (?) working environment.
To Peter, thanks for showing me how it should be done and for being thoroughly BAD!
Ian - what can I say - thanks for being simultaneously the most entertaining and exasperating lab companion ever: CT won't be the same without you!

Away from the lab, I would like to thank Diane for being such a good friend and Alan for giving me advice when I needed it most.

My special thanks to Chris for his love and friendship throughout my time in Bath.

Finally, thank you to my family and in particular to my mother for her gentle support and encouragement over the last seven years.

Contents

Summary

This study investigates the application of ultrasound to the formation of polyurethanes and polylactones. Initial experiments found that ultrasound speeded up the reaction between diisocyanates and diols, giving polyurethanes with higher molecular weights than the thermal/stirred equivalents. Work with the diisocyanate H_{12}MDI revealed that the use of higher ultrasonic intensities resulted in faster polymer formation.

Attempts were made to follow the kinetics of the polyurethane reaction by a number of methods (I.R., gas chromatography, dibutylamine back titration), but inhomogeneity of the reaction mixture made sampling difficult. It appeared however that in a typical ultrasonic reaction, an "initiation" period existed, followed by a sudden "take-off" and the formation of high molecular weight material.

In experiments with the monomers δ-valerolactone and ε-caprolactone, it was found that polylactone formation occurred more quickly when ultrasound was used in addition to heat. Molecular weight studies showed that in ultrasonic experiments, degradation of the polylactones took place and was more pronounced at higher intensities. Experiments were also performed to investigate the effects of omitting catalyst and initiator from the reaction mixture.

Copolymers of δ-valerolactone and ε-caprolactone were synthesised and their structures investigated by ^{1}H NMR. It was found that ultrasonically produced material contained a greater proportion of ε-caprolactone than its thermal equivalent.

CHAPTER ONE

INTRODUCTION

CHAPTER ONE

1.1 Introduction

Until recent years, the methods available for increasing the chemical reactivity of a system could be generalised under the headings below:

(1) Increase the reaction temperature

(2) Increase the concentration of a reagent

(3) Increase the pressure applied to the system

(4) Use a catalyst

However, work in a number of areas of chemistry, including synthesis (organic, inorganic and organometallic) and polymer chemistry has led to the addition of a fifth option to the list:

(5) Irradiate the system with power ultrasound

Ultrasound is the name given to sound having frequencies higher than those to which the human ear can respond (greater than 16 kHz). It is used in medicine, for commercial processes and increasingly in chemical reactions, and may be categorised by reference to its frequency:

(a) High frequency or diagnostic ultrasound (2-10 MHz)

Very low power, typically in the milliwatt range; used for SONAR, by bats for navigation and in medical imaging.

(b) Low frequency or power ultrasound (20-100 kHz)

Much higher power (up to several hundred watts); used in engineering for cutting and grinding and industrially for dispersing solids and forming emulsions e.g. in paint or food manufacture. It is power ultrasound that forms the basis of SONOCHEMISTRY.

Although the effects of ultrasound on chemical processes were studied more than 60 years ago,[1] interest was not widespread. Only since the late 1970's has work in the field been renewed, facilitated by the availability of new ultrasonic equipment. Benefits arising from the use of ultrasound may include increased yield, decreased reaction times, initiation of reactions without the need for additives and the switching to alternative reaction pathways.[2,3]

Most work involving the application of ultrasound to polymer synthesis has concentrated on free-radical polymerisation, so the aim of the current study was to investigate the use of ultrasound in the area of step-growth polymerisation, specifically in the formation of polyurethanes and polylactones. The introduction describes some general polymer chemistry, followed by details of the nature and generation of ultrasound and its effects on chemical reactions. To conclude are descriptions of polylactone and polyurethane chemistry and an outline of the work undertaken in this study.

1.2 General Polymer Chemistry

1.2.1 Nomenclature of Polymers

A polymer is a long molecule formed from a number of repeat units, or monomers, and held together by covalent bonds. If the polymer is made from only one type of monomer then it is known as a homopolymer. If two or more types of monomer are used then it is called a copolymer. The term oligomer is used to describe molecules made up from only a small number of monomers (5 or less).

Depending on the nature of the monomers employed, polymers may be linear, branched or present as a three-dimensional network, as shown below:

linear **branched** **network**

Figure 1.1 Schematic Representation of Different Types of Polymer

The wide range of polymers occurring both naturally and from man-made processes can make classification difficult. A solution is to categorise polymers into groups which reflect their properties and hence often their underlying structure. Three general classes can be defined; thermoplastics, rubbers and thermosets.

Thermoplastics or "plastics" are the largest group and consist of linear or branched polymers which can be melted on the application of heat. Thermoplastics may

be further divided into polymers that crystallise on cooling and those which do not, often finding uses as polymer glasses.

Rubbers are materials which exhibit elasticity i.e. they can be stretched to high extensions and spring back rapidly when the stress is released. This ability results from a lightly cross-linked structure allowing molecules to move past each other on deformation, but not to flow permanently. Rubbers are impossible to melt and only degrade on the application of heat.

Thermosets are rigid and intractable polymers made up from a heavily cross-linked network. Like rubbers, they degrade rather than melt, when heated.

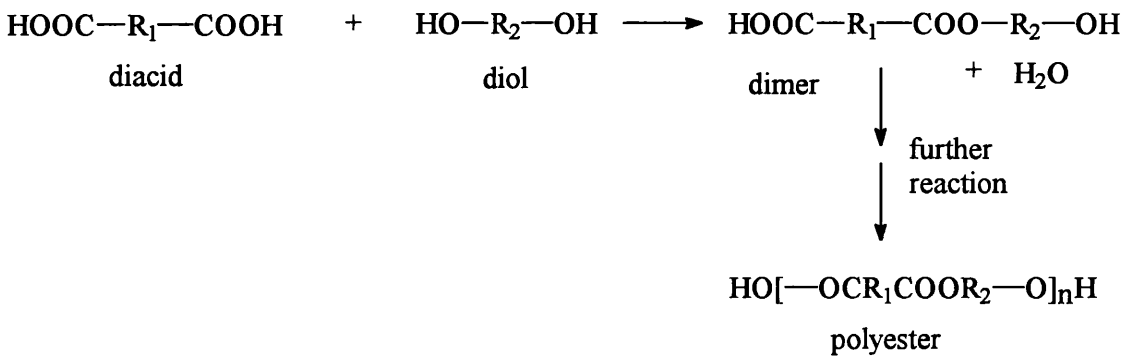
1.2.2 Polymer Formation

The synthesis of polymers is usually divided into two main types;[4] step-growth polymerisation (often called condensation polymerisation) and addition polymerisation. These will be considered in turn.

Step-growth Polymerisation

This type of polymerisation is mainly concerned with condensation reactions between monomers with two or more functional groups. It is characterised by the gradual formation of polymer chains, as dimers produced from monomer reaction go on to react with other dimers or with unreacted monomer molecules.

A general example is given below; the reaction between a diacid and a diol to give a polyester.



The production of a small molecule as a by-product of reaction (in this case water) is common.

Whilst most step-growth polymerisations rely on reaction between two or more types of monomer, an exception is that of ring-opening polymerisation. Here, a reactive species is formed that reacts with and opens a cyclic monomer *via* addition or insertion. Ring-opening polymerisation may be initiated by radical, ionic and coordination/ insertion-type initiators and will be discussed in more detail in Section 1.7.2.

Addition Polymerisation

During addition polymerisation, monomer molecules add to a growing chain one at a time and no small molecules are eliminated. Polymerisation occurs in three distinct steps; initiation, propagation and termination, and monomers usually contain double bonds with the general formula $CH_2=CR_1R_2$. Initiators may be free radical species, cations or anions.

1.2.3 Molecular Weight Averages of Polymers

Many of the properties of a polymer depend on the size of the macromolecules present. Knowledge of "molecular weight" (relative molecular mass) is therefore of

extreme importance.

In natural polymers such as DNA, the macromolecules often have the same number of repeat units (or degree of polymerisation, P). In synthetic polymers however, the statistical nature of preparative methods, means that a distribution of degrees of polymerisation is usual. It is hence not possible to assign a unique molecular weight to a polymer and an average value is quoted. The average value may be defined in a number of ways:[4]

(i) Number Average M_n

This is defined as:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

where n_i is the number of molecules of length i and M_i is the mass of a molecule of length i.

The number average molecular weight of a polymer determines such properties as the brittleness and tensile strength and also affects colligative properties of solution such as osmotic pressure, boiling point elevation and vapour pressure lowering.

(ii) Weight Average

This depends on the weight of polymer chains, w_i, having a particular molecular weight:

$$M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

As each molecule contributes to M_w in proportion to the square of its mass, M_w is greatly influenced by heavier molecular weight species and hence is always greater than M_n, except for monodisperse polymers.

(iii) Other Molecular Weight Averages

Other averages include M_v, the viscosity average and M_z and M_{z+1} which are used to correlate properties such as sedimentation and diffusion. These averages are less frequently used.

Figure 1.2 illustrates a distribution of polymer molecular weight and the relative positions of the molecular weight averages.

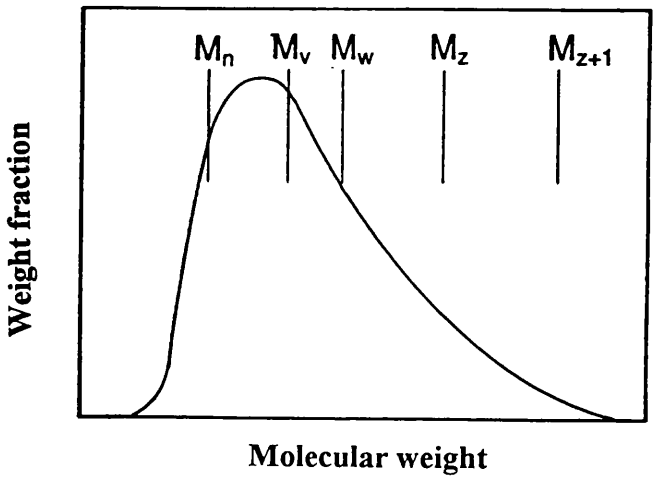


Figure 1.2 Molecular Weight Distribution of a Polymer

Quoting one of the molecular weight averages does not completely characterise a polymer. Two polymers may have the same value of a molecular weight average, but a very different distribution of chain lengths. To overcome this, a polydispersity, γ, is defined such that:

$$\gamma = \frac{M_w}{M_n}$$

A monodisperse polymer will have $\gamma = 1.0$, whilst many common synthetic methods give values around 2.0.[4]

1.2.4 Molecular Weight Determination

There are a number of methods available for the determination of polymer molecular weight averages. These include end group analysis, light scattering, viscometry, ultracentrifugation, gel permeation chromatography and measurement of colligative properties such as ebulliometry, cryoscopy and osmometry.[4]

In this study, polymers were analysed by gel permeation chromatography in order to obtain values for M_n, M_w and γ.

Gel Permeation Chromatography (GPC)

Gel permeation chromatography is a rapid technique for fractionating a polymer. Samples of polymer in solution are injected into a flow of eluent and pumped into a column packed with beads of a range of pore sizes (typically 10-10^5 nm). As the dissolved polymer molecules pass over the porous beads, the smaller polymer chains are able to enter the pores, retarding their flow through the column. Larger molecules are excluded and move more quickly through the column. Figure 1.3 shows how samples are separated according to molecular size.

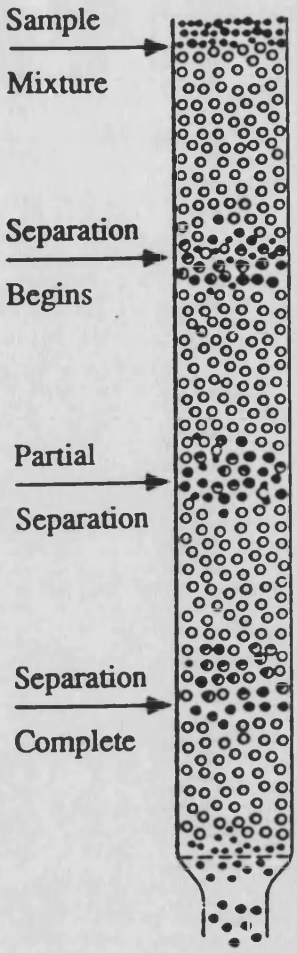


Figure 1.3 Separation of Molecules by GPC

After separation, the concentration of each chain length is measured by either a differential refractometer which compares the refractive index of the column eluent containing the polymer with a reference of pure eluent, or an ultraviolet photometer which is appropriate for a polymer with a significant UV absorbance in a non-absorbing eluent. The recorder output is normally plotted as a function of time or retention volume, V_r.

In order to convert a GPC chromatogram into a molecular weight distribution, it is necessary to know the relationship between molecular weight (M) and V_r. As

molecular size is dependent on M, then V_r can be said to be proportional to a function of M:

$$V_r = f(\log M)$$

GPC is a secondary method of analysis in that it requires calibration with a series of standards of known molecular weight. By plotting a graph of log M against V_r for standards with very narrow molecular weight distributions, an approximate linear calibration is obtained. Figure 1.4 overleaf shows a typical GPC calibration plot.

Calibration standards are available for a number of common polymers including polystyrene, poly(ethylene oxide) and poly(methyl methacrylate). For less common polymers it is not possible to obtain standards and use is therefore made of a "universal calibration". This concept arose from the work of Benoit,[5] who suggested that the molecular size of a material behaving "normally" in solution could be represented by a term known as the hydrodynamic volume of the macromolecule. The hydrodynamic volume is proportional to $[\eta]$ M (where η is intrinsic viscosity). A plot of log ($[\eta]$ M) against V_r is therefore approximately linear and the same for all polymers.

Hence, at any molecular weight:

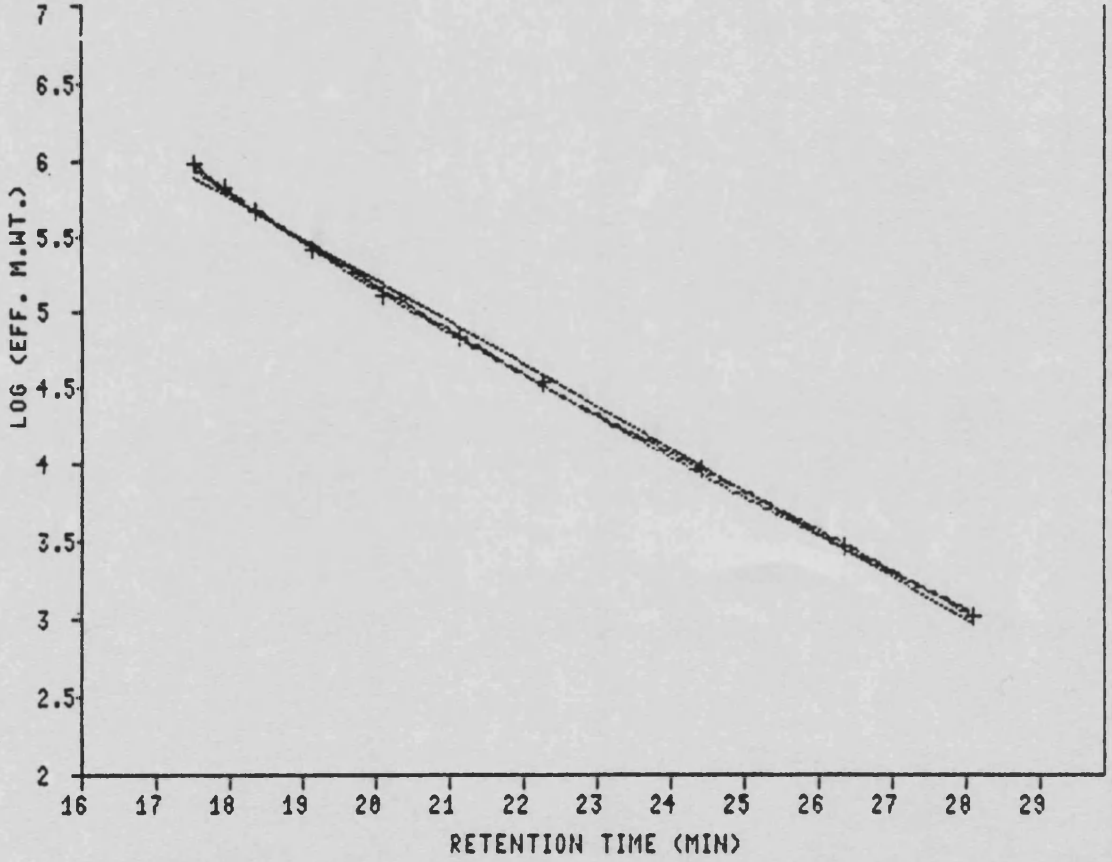
$$[\eta]_s M_s = [\eta]_{unk} M_{unk} \qquad 1.1$$

$$[\eta]_{unk} = \frac{[\eta]_s M_s}{M_{unk}} \qquad 1.2$$

where "s" represents the calibration standard and "unk" the unknown polymer.

Figure 1.4

GPC Calibration Curve



Polynom. 1.Order	
K0	10.6994
K1	-.274167
COR.	.998423
Polynom. 2.Order	
K0	13.052
K1	-.487514
K2	.0047085
COR.	.999629
Polynom. 3.Order	
K0	22.4687
K1	-1.76653
K2	.0618028
K3	-8.37572E-04
COR.	.999925

The well-known Mark-Houwink equation[4] gives the relationship:

$$[\eta] = KM^{\alpha} \qquad 1.3$$

Multiplying both sides by M and substituting for $[\eta]_{unk}$ from equation 1.2:

$$M_{unk}\frac{[\eta]_s M_s}{M_{unk}} = KM_{unk}^{1+\alpha} \qquad 1.4$$

$$\left[\frac{[\eta]_s M_s}{K}\right]^{\frac{1}{1+\alpha}} = M_{unk} \qquad 1.5$$

where K and α are the Mark-Houwink constants for the unknown polymer under the conditions of GPC analysis. By substituting values into equation 1.5 it is possible to obtain "true" molecular weights for polymers by reference to standards, assuming they behave "normally" in solution.

In situations where K and α for the polymer are not known then use of equation 1.5 is not possible. This difficulty may be overcome by carrying out GPC viscometry. This is a relatively new technique[6] in which a viscosity and refractive index detector are used in tandem. The viscosity detector allows determination of $[\eta]$ for the unknown polymer and by manipulation of the Mark-Houwink equation, the GPC processor is able to calculate results for K and α, as shown below:

From 1.3: $$\frac{[\eta]_{unk}}{M_{unk}^{\alpha_{unk}}} = K_{unk} \qquad 1.6$$

$$\ln K_{unk} = \ln[\eta]_{unk} - \alpha_{unk} \ln M_{unk}$$

If $y = c + mx$, then: $y' = m \equiv -\ln M_{unk}$

α_{unk} will lie between 0 and 1, so taking 0.5 as a starting point and using a Newton Iteration, a precise value for α can be calculated:

$$x_2 = x_1 - \frac{f(y)}{f'(y)}$$

$$\text{i.e. } \alpha_{unk} = 0.5 - \left[\frac{\ln[\eta]_{unk} - 0.5 \ln M_{unk}}{-\ln M_{unk}}\right]$$

Once α is known, substitution back in equation 1.6 gives a value for K.

1.3 General Principles of Ultrasound

1.3.1 Generation of Ultrasound

As described in Section 1.1, ultrasound is sound having a frequency greater than the threshold of human hearing (~16 kHz).

Early nineteenth century workers generated ultrasound using mechanical devices which were developments of whistles, sirens or tuning forks.[7] They were limited to low frequencies by modern standards however, with maximum levels of 30-40 kHz. Today, ultrasound is obtained by generating electrical oscillations of the required frequency and

converting them to mechanical oscillations by means of a transducer. The most widespread type of transducer for this purpose is that based on the piezoelectric effect. It operates by the application of an alternating electric potential across opposite faces of a crystal, causing it to vibrate and transmit pressure waves to the surrounding medium.

In order for a material to be piezoelectric, it must be capable of maintaining an electric dipole across its faces. This occurs naturally in quartz when the crystal is sliced along its x or y axes. Other commonly used piezoelectric materials are barium titanate, $BaTiO_3$ and lead niobate, $PbNb_2O_6$,which are prepared as ceramics.[8] Optimum performance of piezoelectric transducers is only obtained at the natural resonant frequency of the sample and for this reason conventional sonochemical equipment operates at a fixed or narrow range of frequencies only.

For applications requiring very high ultrasonic intensities, like cleaning or the use of machine tools, magnetostrictive transducers are common. They utilise materials that change dimension under the influence of a magnetic field e.g. iron or nickel. The transducer takes the form of a rod within a solenoid, which vibrates on the application of a current. Such equipment is limited to a frequency of 100 kHz.

The two main devices available for ultrasound generation in chemical systems are the ultrasonic bath and the ultrasonic probe (or horn). Both make use of piezoelectric transducers.

Ultrasonic Bath

Ultrasonic baths were developed primarily for cleaning purposes and consist of a stainless steel trough with transducers clamped to the base. Reaction vessels are placed directly into water in the bath (Figure 1.5a).

Although relatively economic and easy to use, such baths have severe limitations. Control of acoustic intensity is not possible and the amount of power passing into a reaction vessel will be further determined by factors such as vessel shape and its position within the bath. Acoustic frequency varies from one manufacturers equipment to another, making reproduction of results difficult. During operation, the temperature of water in an ultrasound bath can rise significantly. For accurate work cooling is best introduced by circulating fluid through copper coils suspended in the bath.

The drawbacks outlined mean that ultrasonic baths are used most often when a low ultrasonic intensity is required, or to investigate the qualitative effect of ultrasound on a chemical reaction.

Ultrasonic Probe

Ultrasonic probes are designed to be inserted into reaction vessels, allowing direct transfer of energy to reactants. The attenuation experienced in an ultrasonic bath (where energy has to pass through both water and reaction vessel walls) does not occur, so resultant ultrasonic intensities are much higher.

The probe system is made up of a tapered titanium horn connected to an ultrasound generator (Figure 1.5b). A variety of horn sizes are commercially available.

Figure 1.5a

Ultrasonic Bath

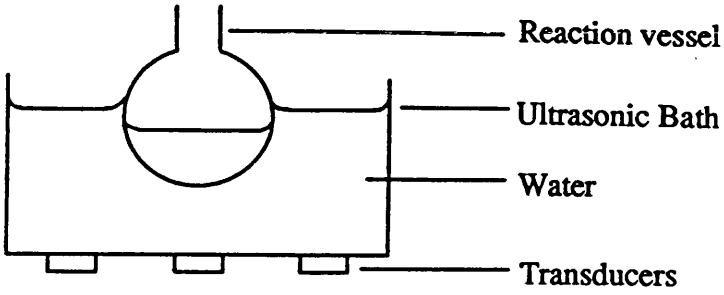
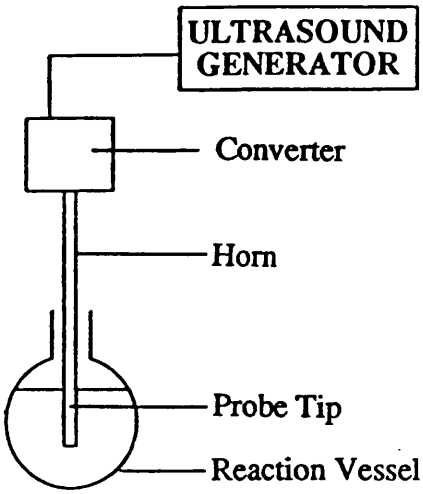


Figure 1.5b

Ultrasonic Probe



Probe intensities are easily and reproducibly variable *via* controls on the generator and the probe may be "tuned" to give maximum performance. Acoustic frequency is fixed, but well defined: most probes operate in the region of 20 kHz.

A disadvantage of prolonged use is the erosion of metal particles from the probe tip. In addition to possible contamination of the reaction mixture, such erosion eventually leads to loss of efficiency. The latter problem can be overcome by periodic replacement of the probe tip.

Temperature rises during sonication may be alleviated by the use of water-jacketed vessels. Vessels can also be adapted for experiments under inert atmospheres or moderate pressure.

1.3.2 Wave motion of Ultrasound

Ultrasound (like all sound), is transmitted through a medium by the displacement of particles from their equilibrium position. Waves can therefore be propagated in any solid, liquid or gas possessing elastic properties. In liquids and gases, particle oscillation takes place in the direction of wave propagation i.e. the motion of ultrasound is longitudinal rather than transverse.

As an ultrasonic wave passes through a medium, there will be places where molecules are compressed and pressure is higher than normal. Conversely, in regions where molecules are pulled apart, pressure is lower than normal. The equation below represents this motion, with P_A being acoustic pressure at time t and f being the frequency of the ultrasound.

$$P_A = P_{max} \sin 2\pi ft$$

The intensity of an ultrasonic wave is defined as the energy transmitted through unit area in unit time. It is measured in Wm^{-2} and is given by:

$$I = \frac{P_{max}^2}{2\rho c}$$

where c is the velocity of sound in the medium and ρ is the density of the medium.

As a wave travels it will be attenuated as energy is given up to the surroundings. The main factors influencing the attenuation of ultrasound in a medium are viscosity, thermal conductivity of the medium and thermal relaxation. Thermal relaxation refers to the transformation of ultrasonic energy into rotation and translation of the molecules involved. Attenuation can be represented by the equation below, where α, the absorption coefficient depends on the factors mentioned above and I_d is the intensity of sound at a distance d from a source radiating with intensity I_o.

$$I_d = I_o \exp(-2\alpha d)$$

The speed of ultrasound passing through a medium will depend on its density (ρ) and elasticity (ε), as shown by the following equation:

$$c = \sqrt{\frac{\varepsilon}{\rho}}$$

Some values for c in different liquids are given below, together with approximate ultrasonic wavelengths (assuming generation at 20 kHz).[7]

Liquid	Speed of Ultrasound ($m\ s^{-1}$)	Wavelength (cm)
Distilled Water	1482	7.4
Acetic Acid	1173	5.9
Acetone	1190	6.0
Carbon Tetrachloride	940	4.7
Ethanol	1162	5.8
Glycerol	1860	9.3
Mercury	1454	7.3

1.4 Ultrasonic Cavitation

1.4.1 Formation of Cavitation Bubbles

"Cavitation" refers to the formation and subsequent dynamic life of bubbles within liquids and is a very important ultrasonic phenomenon.

As previously described, the passage of an ultrasonic wave through a liquid gives rise to areas of negative pressure as molecules are pulled apart. If the pressure is sufficiently large, then the distance between the molecules will exceed the critical distance necessary to hold the liquid intact and it will break down, creating cavities. The cavitation process is aided by the presence of "weak spots" or nucleation centres in the liquid, which lower its tensile strength. These include gas molecules[9] and suspended solid particles.[10]

Flynn[11] proposed in 1964 that cavitation could be classed as stable or transient. Transient bubbles exist for only a few acoustic cycles, expanding to a radius of at least twice their original size before collapsing violently, Stable bubbles are believed to

contain dissolved gas and/or solvent vapour which help to prevent immediate collapse. Such bubbles gradually grow in size to a diameter of 100-200 μm, whereupon they come into resonance with the sound field and undergo rapid expansion and collapse. Figure 1.6 is a schematic representation of the cavitation process.

Ultra-high-speed photography has recently enabled observation of bubble formation.[12,13] An example is given in Figure 1.7, which is a series of photographs showing the ultrasonic growth and collapse of a bubble near a solid boundary.[13] It can be seen that collapse is asymmetric, with a "jet" of liquid emerging from the bubble towards the solid surface.

Theoretical considerations by several workers[11,14] have led to estimations of the temperatures and pressures occurring during the collapse of cavitation bubbles. Noltingk and Neppiras[14] showed that the final temperature and pressures generated can be expressed by the following equations, assuming adiabatic bubble collapse:

$$T_f = T_o [P_m (\gamma-1) / P]$$

$$P_f = P [P_m (\gamma-1) / P]^{\gamma/(\gamma-1)}$$

T_o is the bulk temperature of the liquid, P_m is the pressure in the bubble after collapse, P is the pressure before collapse, usually assumed to correspond to the solvent vapour pressure and γ is the ratio of specific heats of the vapour or any dissolved gas. Depending on the liquid and the precise conditions used, these equations predict values of 1000-2000 bar for P_f and 4000-6000 K for T_f.

Figure 1.6

Schematic Representation of the Cavitation Process

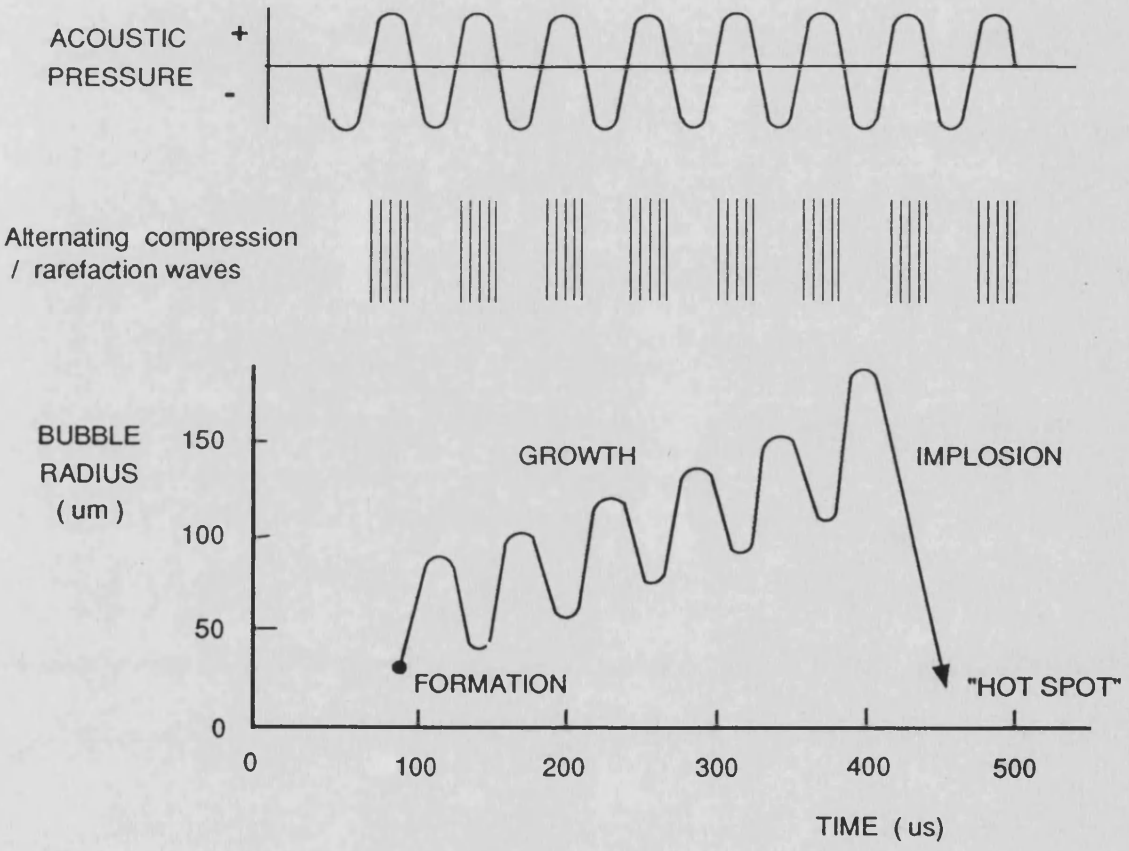
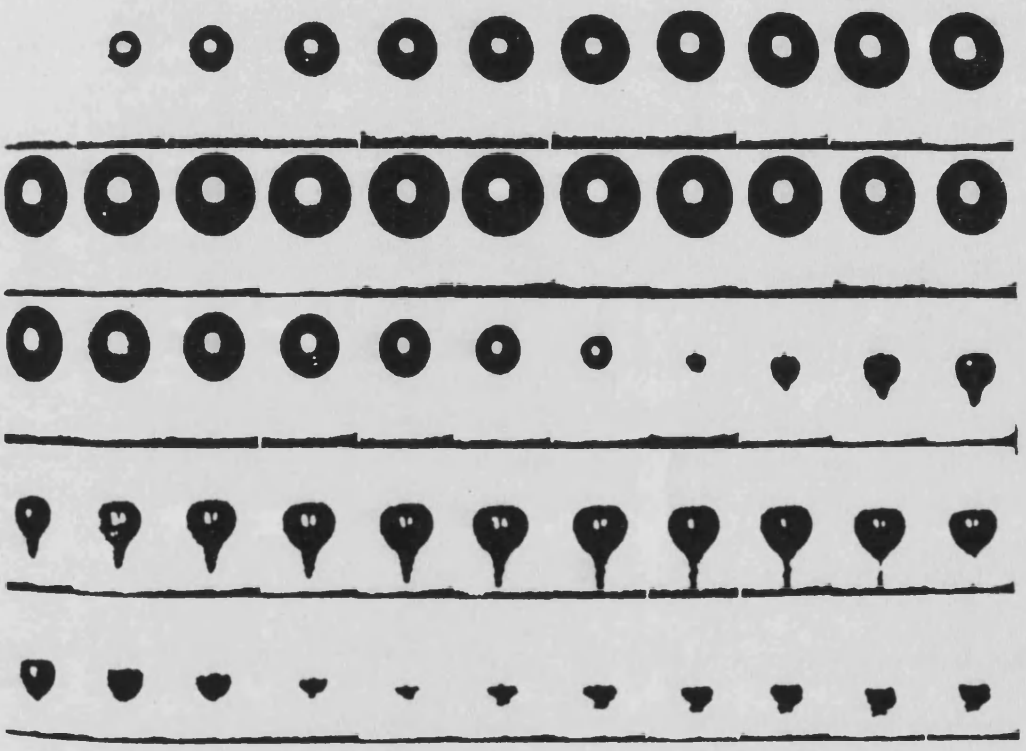


Figure 1.7

The Collapse of a Cavitation Bubble near a Solid Boundary



There is now considerable evidence to support this so called "hot-spot" theory. Verrall[15] and more recently Suslick and co-workers,[16] have measured the spectra of species arising from sonoluminescence (short flashes of light emitted during cavitation). The spectra from alkane solvents are very similar to those from species involved in combustion at several thousand Kelvin.

Some workers however have proposed an alternative to the "hot-spot" process, namely an "electrical" theory. Margulis *et al* [17] have considered the charge distribution due to the alignment of dipoles around a cavitation bubble and suggest that extremely large electrical fields of the order of 10^{11} V m^{-1} can be generated. Their discharge may be likened to lighening flashes, which have sufficient energy to cause bond breakage and chemical activity.

1.4.2 Factors Affecting Cavitation

As many of the chemical effects of ultrasound can be traced back to cavitation, it is important to understand some of the factors affecting the cavitation process in a liquid.[18,19]

Ultrasonic Intensity

As the ultrasonic intensity (i.e. the amplitude of the sound wave) is increased, a larger number of cavitation bubbles are produced and their radii increases. This leads to bubble collapse of a greater violence.[20] However, the intensity cannot be increased indefinitely, as larger bubbles have insufficient time to collapse during the ultrasonic cycle. It has been found that optimum intensities exist for many sonochemical processes, above which the benefit falls.[21]

Ultrasonic Frequency

Although the effect of altering ultrasonic frequency has not been widely investigated, it has been found that cavitation is suppressed at very high frequencies.[22] Eyring[23] suggested that as the time between ultrasonic cycles decreases, there was insufficient time for cavitation bubbles to grow. Some recent work[24] has shown that oxidation reactions proceed faster at higher frequencies, but that an optimum value exists.

Solvent

As cavitation depends on the movement of solvent molecules, factors such as viscosity, density and surface tension will affect the growth of bubbles. The use of solvents with a low surface tension for example, has been found to lead to a reduction in the cavitation threshold (i.e. the ultrasonic intensity at which cavitation is first detected).[25]

Solvent vapour pressure is also particularly important. When the volatility of a solvent is high, more vapour will diffuse into cavitation bubbles, "cushioning" their collapse and reducing associated effects.[11]

Dissolved Gases

Gases with high solubility will provide many nucleation sites within the liquid and thus lower the cavitation threshold. However, gas molecules will also be more likely to pass into cavitation bubbles, "cushioning" collapse in a similar manner to solvent vapour.[26]

Temperature

Sonochemical systems are of particular interest as they do not obey the usual Arrhenius relationship and often proceed with higher rates at lower temperatures. This is mainly due to increased solvent volatility at higher temperatures, which leads to cavitation "cushioning" as already described.

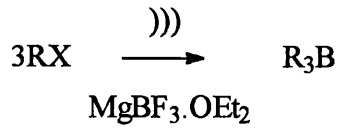
1.5 Effects of Ultrasound on Chemical Reactions

In recent years ultrasound has been applied to many different types of chemical reaction, often giving improved yields and decreased reaction times.[2] As the current study is concerned with polymer chemistry, attention will be focused on work in that area. The first section however gives a brief survey of general ultrasonic effects.

1.5.1 Characteristics of Ultrasonic Reactions

Ultrasound has proved beneficial in many heterogeneous reactions, in particular those involving metals.[2] This is due mainly to the collapse of cavitation bubbles and the subsequent ejection of liquid jets (as in Figure 1.7). The resultant agitation is effective in breaking and dispersing particles within solution, increasing the surface area available for reaction. Enhanced mixing also removes inhibitors, impurities and products from catalyst/reactant surfaces, giving a greater number of available reaction sites.

Many hundreds of heterogeneous reactions have been performed using ultrasound. An example is the synthesis of organoboranes from Grignard reagents and borontrihalides in ether:[27]



The reaction is normally performed by stirring, but the use of ultrasound results in a 50-fold increase in reaction rate.

Homogenous ultrasonic reactions have also received much attention.[2] Reactions in aqueous solution have proved particularly interesting, due to the ability of ultrasound to break down water molecules to give OH and H radicals.[28] Sonication of organic compounds in aqueous solution leads to a variety of breakdown products, some arising from secondary reactions of OH and H radicals e.g. sonication of CCl_4 gives Cl_2, CO_2, HCl, C_2Cl_6 and HOCl.[29] Sonication of "neat" organic liquids also gives breakdown products and radical species, with alkyl-halide bonds being particularly prone to scission.[2]

The precise cause of ultrasonic bond cleavage is uncertain, but it is known that species exist in high energy, vibrationally excited forms, inside collapsing cavitation bubbles. Three "zones" can be identified within a system; the centre of the bubble containing the reactive species formed under the harsh conditions, the bulk liquid in which no primary sonochemical activity takes place, although subsequent reaction with sonochemically generated species may occur, and finally the interfacial region where there are large temperature and pressure gradients. Experiments performed by Suslick with volatile metal carbonyls[30] suggested that reaction occurred both within the cavitation bubbles and at the bubble-liquid interface.

1.5.2 Ultrasonic Polymer Degradation

Before considering ultrasonic polymer synthesis, it is necessary to describe the effects of ultrasonic degradation on polymer chains.

The reduction in molecular weight of polymers is one of the oldest known sonochemical processes, with workers in the 1930's reducing the viscosity of natural polymers such as starch and gum arabic.[31,32] In recent years the degradation process has been well studied and its effects are seen in a wide range of organic and inorganic polymers in both organic and aqueous solution.[33]

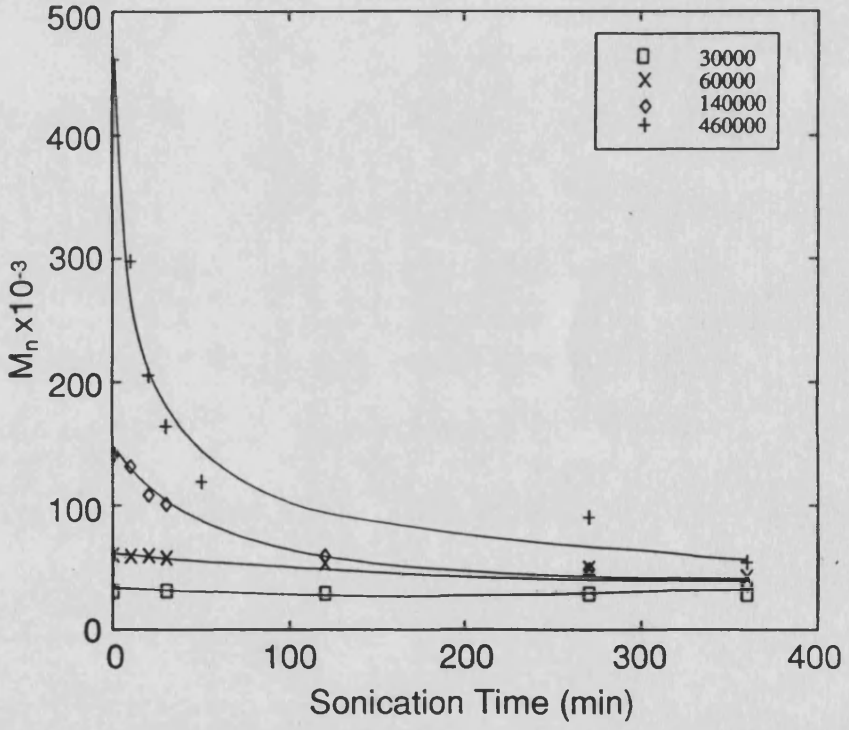
Ultrasonic degradation is characterised by a narrowing in polydispersity and a decrease in polymer molecular weight down to a limiting value, M_{lim} below which no further degradation occurs.[34] The degradation proceeds more effectively at higher molecular weights as illustrated in Figure 1.8.[35]

There is some debate as to the exact nature of polymer degradation, but it has been shown to be a direct consequence of cavitation. Under conditions which suppress cavitation no degradation has been found.[36]

The mechanism can be best described as the polymer chain being caught in the rapid flow of solvent molecules caused by the collapse of cavitation bubbles. Shock waves generated after bubble implosion also produce violent solvent movement. Polymer chains are therefore subjected to extremely large shear forces which can cause bond breakage as shown schematically in Figure 1.9.[33] Some workers have also interpreted the effect in terms of frictional forces between the solvent molecules and polymer chains.

Figure 1.8

Variation of the Number Average Molecular Weight during the Sonication of 0.5% w/v Polystyrene Solutions in Toluene



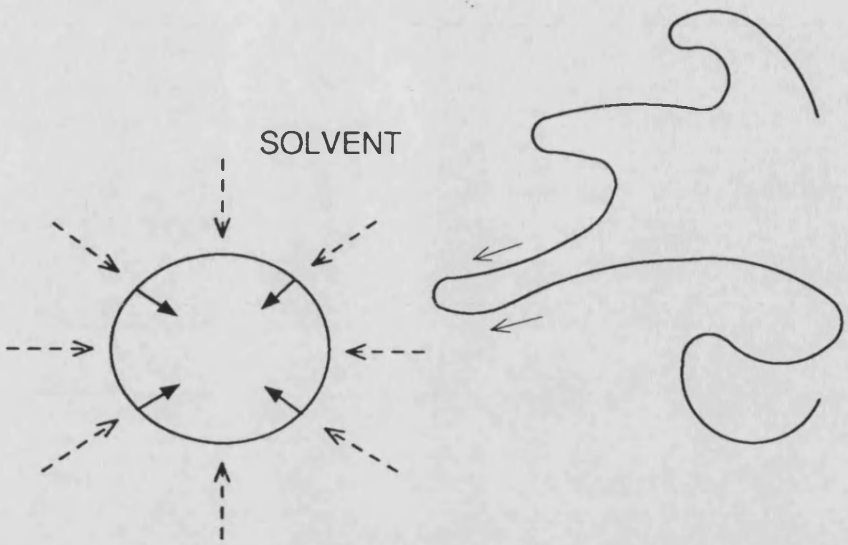


Figure 1.9 Schematic Representation of Cavitationally Induced Polymer Degradation

It might be thought that the extreme temperatures found in cavitation bubbles would contribute to degradation, however no evidence of thermal breakdown products (i.e. monomers) has been found. It is usual for thermal degradation to produce chain cleavage in a random manner but a number of workers have shown that ultrasonic cleavage occurs preferentially near the middle of the chain.[37,38]

1.5.3 Radically Initiated Ultrasonic Polymerisation

The use of radical initiators is the most common method of polymerisation of vinyl monomers. As mentioned in Section 1.5.1, irradiation of water leads to the production of OH and H radicals. Lindstrom and Lamm[39] made use of this effect to produce polyacrylonitrile in aqueous solution.

Although it was originally thought that ultrasonic polymerisation would not occur in organic systems unless an initiator was present or the mixture was "seeded" with preformed polymer,[40] it has become clear in recent years that vinyl monomers can be polymerised solely by ultrasonic irradiation i.e. ultrasound is able to form radicals in vinyl species.

Kruus and co-workers[41-43] produced poly(methyl methacrylate) and polystyrene without initiator and found that polymerisation ceased when the ultrasound was switched off. With longer reaction times a decrease in molecular weight was seen as ultrasonic degradation began to affect the newly formed polymer chains.

Price *et al.* [44,45] investigated the rate of ultrasonic initiation of methyl methacrylate and estimated that at room temperature ultrasound produced radicals at a similar rate to that expected from an initiator at 70°C. Study of the polymer propagation however led to the conclusion that ultrasound had little significant effect on this stage of the reaction.

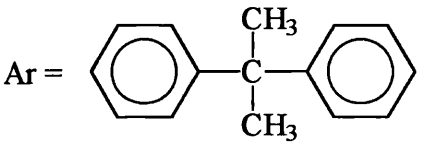
As described in Section 1.5.2, ultrasound causes ready polymer degradation in solution. This is apparent in ultrasonic polymerisation experiments, where high molecular weight polymer is formed during the early stages of reaction, followed by an exponential fall in weight at longer reaction times to a limiting value.[44]

Ultrasonically initiated vinyl polymers may be useful in special cases where the absence of initiator fragments is required e.g. in poly(methyl methacrylate) dental fillings.[33] The occurrence of degradation is also important when precise control is required over polymer molecular weight. Finally, the ability to perform reactions at low

temperatures and to "switch off" initiation by stopping ultrasound generation may have uses in commercial situations.[33]

1.5.4 Ultrasonically Promoted Step Growth Polymerisation

There are very few reports of the application of ultrasound to conventional "condensation" reactions. Watanabe *et al*[46] used an ultrasonic bath to prepare aromatic polyformals from, for example, bisphenol-A and methylene bromide. This is a two phase reaction for which a phase-transfer catalyst (tetrabutyl ammonium bromide, TBAB) is necessary.

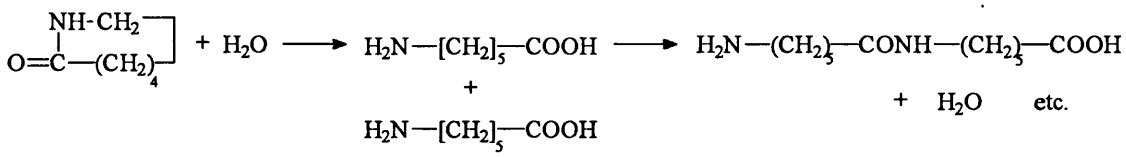


Sonicated reactions gave higher yields of polymers with much larger inherent viscosities. No reaction occurred in the absence of the phase transfer catalyst however, suggesting that the role of ultrasound was to promote catalyst dispersion and also to move reactants rapidly over the surface of the powdered potassium hydroxide.

On a larger scale, Long[47] in a patent, described reaction vessels incorporating ultrasonically vibrating walls which were used to control both when and where polymerisation took place in several polyurethane systems. The arrangement was especially useful for producing foams.

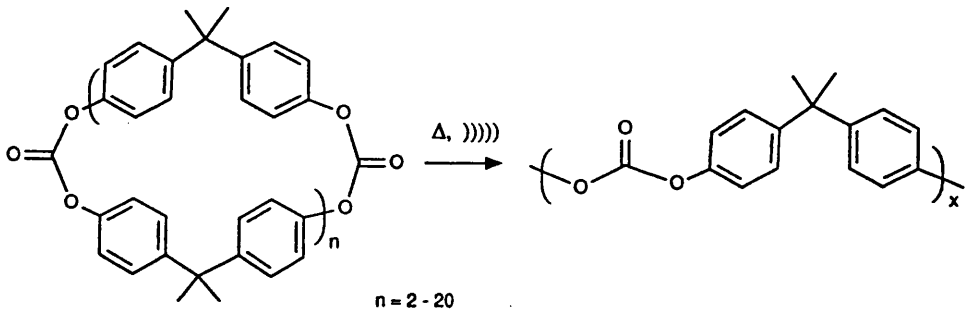
A little more work has been performed in the area of ring-opening polymerisation.

Ragaini *et al* have studied the ultrasonic reaction of ε-caprolactam to give Nylon-6.[48,49] Conventionally, a small amount of water (~1%) is added to the monomer to initiate ring-opening, followed by a polymerisation reaction under vacuum.



Ultrasound was found to allow single-step polymerisation without the need to add water. High molecular weight materials with narrower polydispersities were formed in shorter reaction times than in the conventional process.

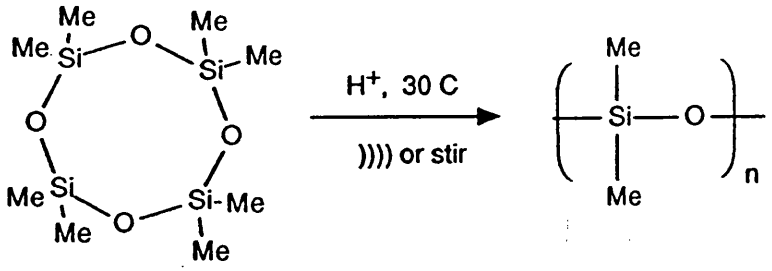
More recently, Stoessel[50] reported the use of ultrasound at very high intensities in the ring-opening of polycarbonate oligomers.



Polymerisation in the above system is normally initiated by nucleophiles (e.g. metal carbonates) at high temperatures, but it was found that using ultrasound, an initiator was not always required and that it was possible to perform experiments at lower

temperatures. Stoessel suggested that polymerisation resulted from high local cavitation temperatures or from the sonochemical promotion of impurities such as sodium hydroxide.

A final example of the application of ultrasound to a ring system is in the production of poly(dimethyl siloxane) (PDMS) from octamethylcyclotetrasiloxane, catalysed by sulphuric acid.



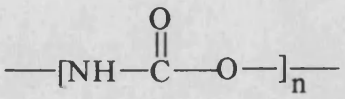
Price *et al.*[51] found that although ultrasound was unable to initiate ring-opening in the absence of added catalyst, the resultant polymer had a narrower polydispersity than its thermal equivalent and unexpectedly a higher molecular weight (degradation normally leads to a narrower polydispersity and a reduction in molecular weight).

In conclusion, the application of ultrasound to polymerisation reactions can give increased reaction rates and yields and (particularly in vinyl polymerisation) can obviate the need for an initiator. The most useful benefits however are likely to come from accurate contol of polymer molecular weight and polydispersity, particularly in the production of specialist materials.

1.6 Polyurethanes

1.6.1 Basic Chemistry

The generic name "polyurethane" refers to polymers with urethane linkages in the chain.



Urethane Link

The original discovery of polyurethanes was made by Otto Bayer in 1937, who was looking for materials to compete with the newly produced polyamides or nylons of Du Pont USA. Today, their unique combination of properties and ability to be processed and shaped by almost all known manufacturing techniques have led to their use in a number of end products. In particular, this versatility is based on the ability to synthesise polymers containing not only the urethane link, but also other groups as units in the polymer chain. Figure 1.10 below gives examples of the range of polymers available by varying physical characteristics.

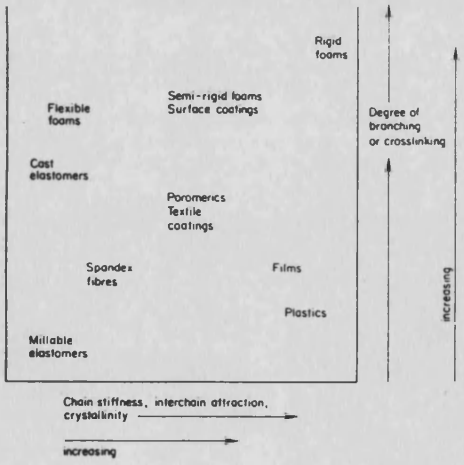
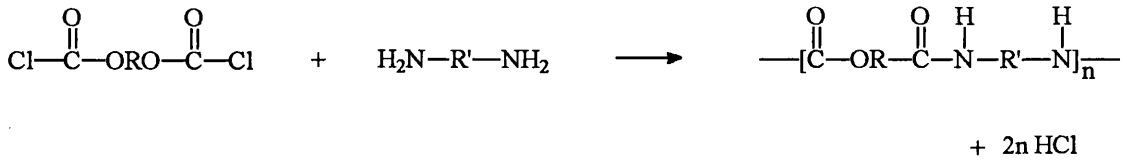
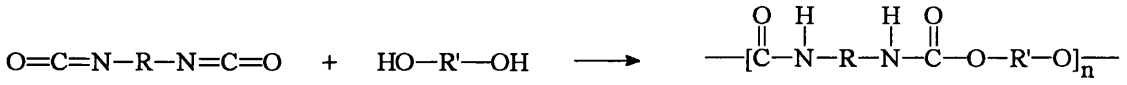


Figure 1.10 Structure-Property Relationships for Polyurethanes

Polyurethanes are examples of step-growth polymers and are formed as a result of reaction between monomer functional groups. There are two main preparative methods available. The first is the condensation reaction of a bischloroformate with a diamine:



The second option is the reaction between a diisocyanate and a diol or other OH-terminated compound. Unusually for a step-growth polymerisation, no condensate or by-product is produced:



It is the second reaction which is of greatest importance industrially and on which this study will concentrate.

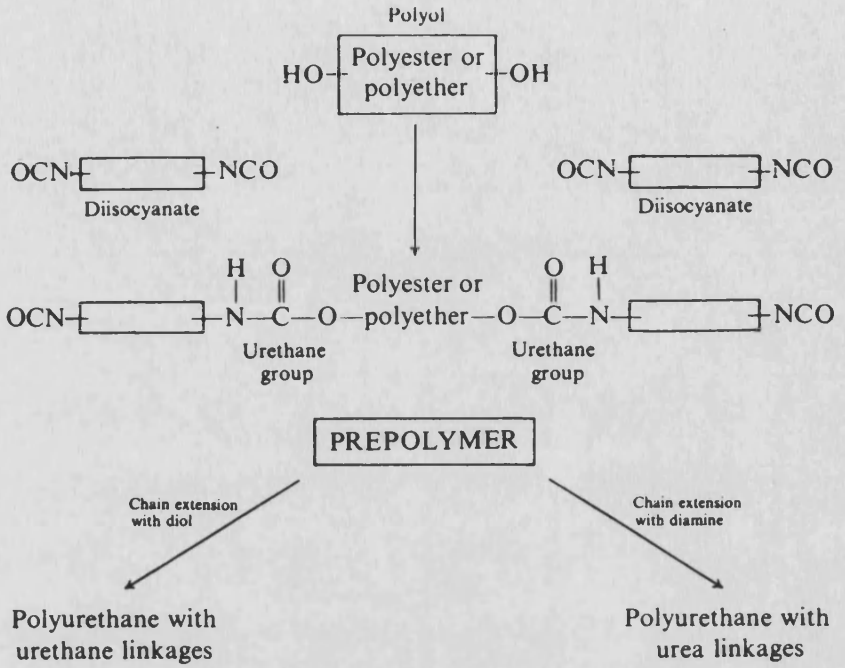
1.6.2 Structure and Formation of Polyurethane Elastomers

A urethane elastomer can be regarded as a linear block copolymer comprised of three blocks; the polyol (hydroxy-terminated polymer), diisocyanate and chain extender (short chain diol or amine). These may be reacted together by either of two methods, the "prepolymer" route or the "one shot process" (Figure 1.11).

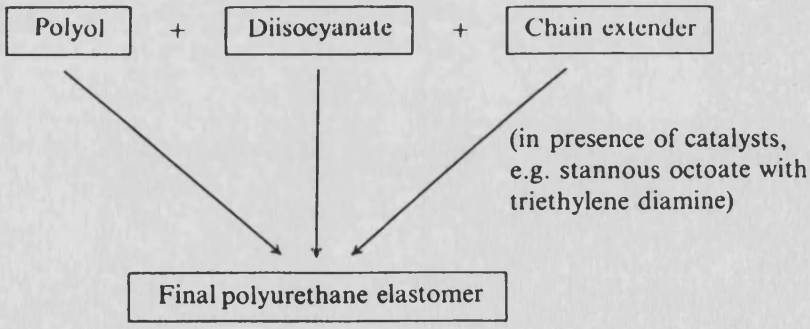
The prepolymer method is the usual route. Initially the diisocyanate and polyol are reacted together to form an intermediate polymer of molecular weight 15000-20000,

Figure 1.11

Preparative Routes for Polyurethanes



Prepolymer Route



One-shot Process

which is called a "prepolymer". This is normally a thick, viscous liquid or low melting-point solid. The prepolymer is converted into the final high molecular weight polymer by further reaction with a diol or diamine chain extender.

Alternatively, the entire polymer formation may be carried out by simultaneously mixing together all three components in the presence of a catalyst e.g. an organo-tin compound.

The isocyanate linkage imparts rigidity to the chain, whilst the polyol is a flexible block. This is illustrated below.

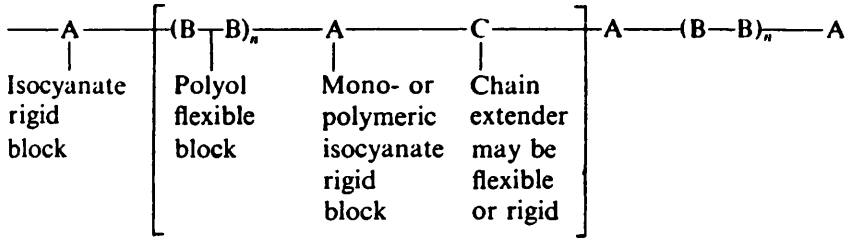


Figure 1.12 Basic Unit in a Urethane Block Copolymer

Evidence from X-ray diffraction suggests that the flexible segments are between 1000-2000 nm long and the rigid units are shorter (150 nm), with hydrogen bonds between adjacent chains. The orientation of the segments is shown in Figure 1.13.

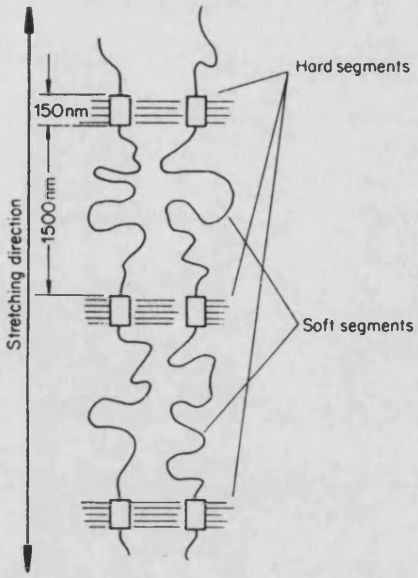


Figure 1.13 Flexible and Rigid Segments in a Polyurethane Elastomer

If water is present in the reaction mixture, it acts as a nucleophile like other hydroxyl compounds. Its reaction leads to an unstable product which decomposes to give carbon dioxide and an amine. The bubbles of CO_2 released within the mixture give rise to a foam product.

$$R{-}NCO + H{-}OH \longrightarrow \underset{\text{carbamic acid}}{R{-}\overset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}OH} \longrightarrow R{-}NH_2 + CO_2$$

1.6.3 Property-Structure Relationships

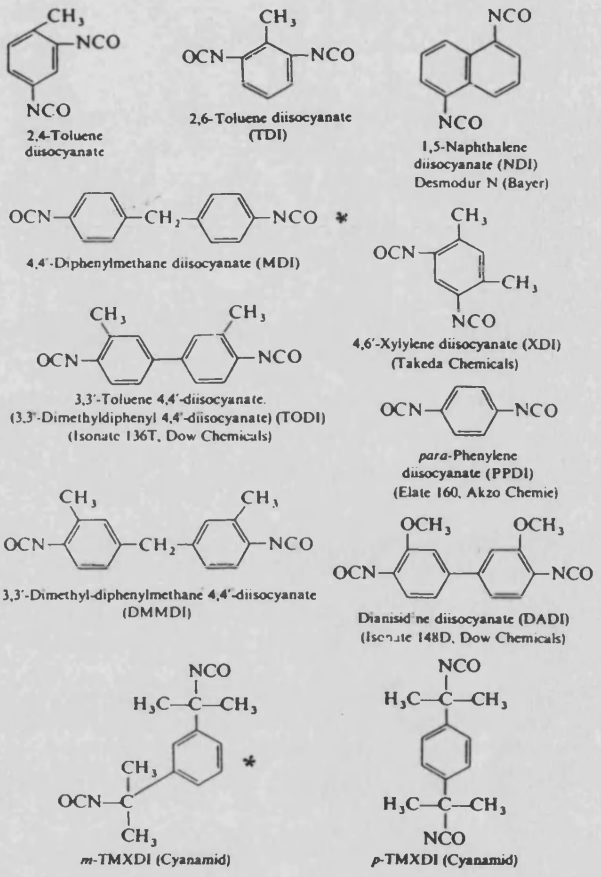
The nature of the three different polyurethane blocks will be considered in turn.

Diisocyanates

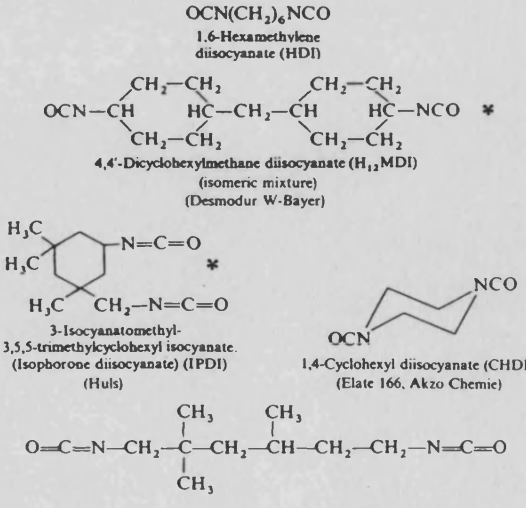
Examples of diisocyanates, both aromatic and aliphatic, used in polyurethane elastomer synthesis are shown overleaf. Those marked with an asterisk were used in this study.

Figure 1.14

Diisocyanates used in Polyurethane Synthesis



Aromatic



Aliphatic

As illustrated in Figures 1.12 and 1.13, isocyanates are responsible for the rigid segments of an elastomer and the resultant interchain interactions. Preferred isocyanates are those having large molecular structural bulk which gives rise to interchain steric hindrance and hence high levels of modulus and tensile strength.

When comparing aliphatic with aromatic diisocyanates, it is usually found that elastomers based on aliphatic species exhibit improved light stability as well as better resistance to hydrolysis and thermal degradation.[52] Additionally, H_{12}MDI elastomers have been found to have better mechanical properties than their aromatic MDI analogues.[53]

Polyols (Hydroxy-terminated Polymers)

Aliphatic polyethers or polyesters are the normal materials used as flexible segments in commercial elastomeric polyurethanes. Some examples of commonly used compounds are given in Figure 1.15.

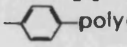
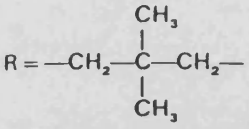
These materials have glass transition temperatures below room temperature and are low melting-point solids or liquids, with a molecular weight from 600-3000. Higher molecular weights give materials with better tensile properties but with an increasing tendency to cold-harden.

Polyethers have weaker interchain forces than polyesters and generally give elastomers with somewhat inferior physical properties. They show better resistance to hydrolysis however, as a result of the superior hydrolytic stability of ether groups over esters.

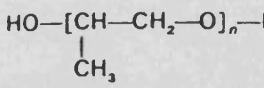
Figure 1.15

Polyols used in Polyurethane Synthesis

POLYESTERS USED IN PU ELASTOMER SYNTHESIS

General structure:	$HO—R—[O—CO—R'—CO—O—R]_n—OH$
$R = —(CH_2)_2—$;	$R' = —(CH_2)_4—$poly(alkylene) adipates
$R = —(CH_2)_4—$;	$R' = —(CH_2)_8—$poly(alkylene) sebacates
$R = —(CH_2)_6—$;	$R' =$  poly(alkylene) benzoates
	
$R = —(CH_2)_2—O—(CH_2)_2—$	

POLYETHERS USED IN PU ELASTOMER SYNTHESIS

$HO—[(CH_2)_4—O]_n—H$	Poly(tetramethylene-ether) glycols used for high strength elastomers; expensive
	Poly(oxypropylene) glycols used for lower strength elastomers; lower cost

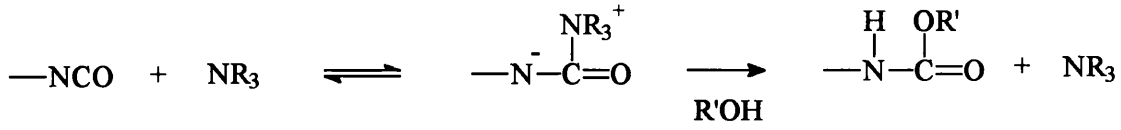
Chain Extenders

Chain extenders are typically low molecular weight diols or diamines. When a diamine is employed as an extender, a higher level of physical properties usually results, due to the production of urea linkages which enter into strong hydrogen-bonded interactions. In particular, diamines are used with unsymetrical diisocyanates whilst diols give elastomers of good strength with symmetrical diisocyanates.

1.6.4 Catalysis

Two particular classes of compound are important for the catalysis of polyurethane reactions; amines and organic metal salts.

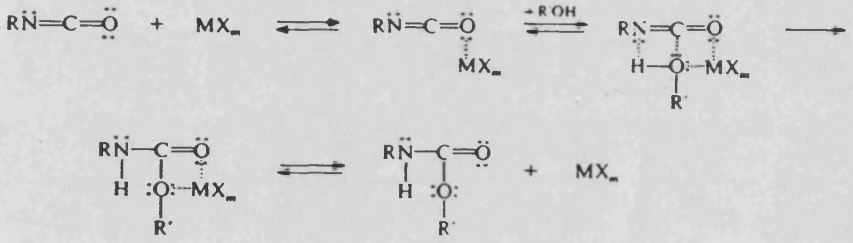
The method by which amines promote isocyanate-hydroxyl reactions was first investigated by Baker and Holdsworth.[54] They proposed that the catalyst formed a complex with the isocyanate which subsequently reacted with the hydroxyl compound, regenerating the amine.



Baker and Holdsworth also investigated the effect of changing the basicity and steric nature of the amine.[54] In common with many subsequent studies, it was found that catalyst efficiency generally increased with increasing basicity of the amine and decreased with increasing steric shielding of the amine nitrogen.

Examples of amine catalysts include tetramethyl ethyl diamine (TMEDA) and triethyl diamine (DABCO). Tertiary amines are particularly effective at promoting the water-NCO reaction and as a result are often used in foam production.

Stronger catalysis for polyurethane formation is provided by organometallic compounds, especially organotin species. Although their mechanism of action is not completely understood, they seem to act by forming complexes involving the catalyst itself, the isocyanate and the hydroxyl compound. Complex formation leads to an increased electrophilicity of the isocyanate carbon and "brings closer" the NCO and OH species. One formal mechanism is suggested below.[55]



Dibutyltin dilaurate and stannous octoate are amongst catalysts commonly used. Figure 1.16 shows the rate enhancements available using a variety of catalysts (the uncatalysed reaction having a relative rate of 1).[53] Combinations of tin catalysts with tertiary amines can be seen to give a synergistic increase in catalytic activity.

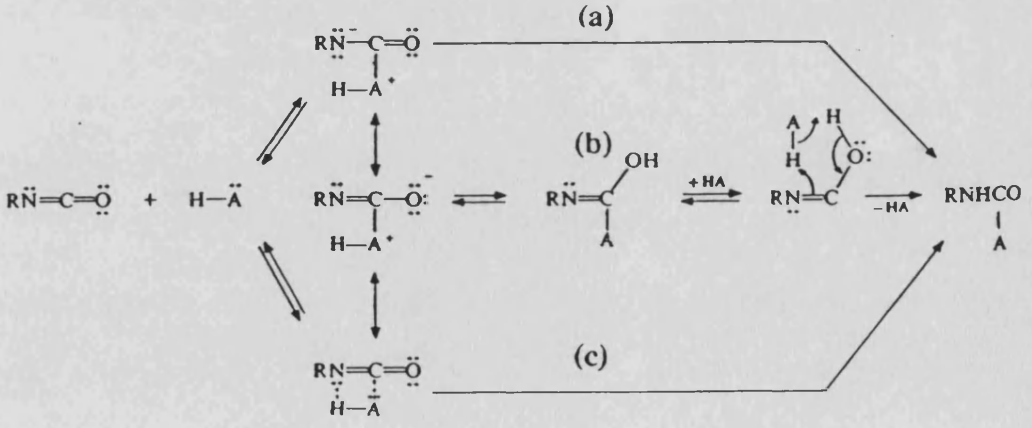
Catalyst	*Concentration (%)*	*Relative rate*
None	—	1
N,N,N',N'-Tetramethylbutanediamine (TMBDA)	0·5	160
Triethylene diamine (DABCO)	0·2	260
Triethylene diamine	0·3	330
Dibutyltin dilaurate (DBTDL)	0·1	210
Sn(II) octoate	0·1	540
DBTDL + TMBDA	0·1 + 0·2	700
Sn(II) octoate + TMBDA	0·1 + 0·2	1000
DBTDL + DABCO	0·1 + 0·2	1000
Sn(II) octoate + DABCO	0·1 + 0·2	1510

Figure 1.16 Relative Reaction Rates of Catalysts on the NCO-OH Reaction

1.6.5 Reaction Rates

A variety of mechanisms and kinetic schemes have been proposed for polyurethane formation.[56] It is first necessary however to consider the reaction between mono-isocyantes and mono-alcohols.

When uncatalysed, three different pathways have been proposed,[57] as illustrated below.



A = nucleophile atom of the reactant

Baker,[54] in 1947 was the first to study this type of system. He performed solution experiments with methanol and aryl isocyanates and suggested that the reaction proceeded by a second order process i.e.

$$\frac{-d[NCO]}{dt} = \frac{d[urethane]}{dt} = k[NCO][OH]$$

His findings have been confirmed by a number of other workers in the field.

It is often the case however, that the rate constant k increases during the course of an experiment, due to a moderate catalytic effect by the newly formed urethane which behaves as a weak base. Baker also found an increase in the rate constant with an increase in the alcohol concentration of the reaction mixture (OH is a very weak base). The order of the reaction with respect to [OH] is therefore somewhat greater than one. It is questionable as to whether a truly uncatalysed NCO-OH reaction does exist at all.

When a catalyst is added to a mono-isocyanate-mono-alcohol reaction then, as expected, there is an effect on the reaction kinetics. Wong and Frisch[58] reacted phenyl isocyanate with butanol in acetonitrile, using a number of catalysts. The dibutyltin dilaurate reaction was found to follow second-order kinetics to about 80% conversion, whilst a number of amine-catalysed reactions gave approximately first order rates to 90% conversion.

Uncatalysed polyurethane reactions (i.e. those using di-functional rather than mono-functional monomers) are generally found to be second order, in a similar manner to the simple reactions already described.[59,60] As with the mono-functional reactants however, a number of factors can affect the reaction order.

Side reactions are often found to accompany polyurethane formation, namely; trimerisation of the isocyanate component to yield an isocyanurate, dimerisation to form a carbodiimide, and occasionally allophanate cross-linking (reaction of an isocyanate group with a urethane group). Krol[61] found that the reaction between TDI and butanediol followed second order kinetics up to 60-70% conversion, after which time a slight decrease in the rate constant was observed. He attributed this to the influence of side reactions.

The nature of the monomers is also important in determining kinetics. Reactions involving polyesters and polyethers proceed more quickly than those using simple diols, whilst primary species,(rather than secondary),[62] are particularly reactive. Investigation into the reactivity of aromatic diisocyanates[63] has shown that the second isocyanate group exerts a substantial influence on the reactivity of the first. For example, an aromatic diisocyanate with the isocyanate group meta or para to the other results in about a six-fold increase in the initial rate constants. As the reaction proceeds however, the urethane group formed in the reaction becomes the influencing group and the rate constant decreases. This is because the urethane group is less activating than the original isocyanate.

The role of the solvent is another consideration in polyurethane reactions. Solvents of increasing dielectric constant (i.e. more powerfully hydrogen bonded), tend to slow polyurethane formation by virtue of a higher association with the hydroxyl group. This opposes the NCO-OH interaction.[64] Further complications arise when polymerisations are performed in bulk or in concentrated solution and diffusion kinetics play a role in determining reaction rate.

Finally, the presence of a catalyst (as described in Section 1.6.4) is of major importance.

It must therefore be borne in mind when studying polyurethane reactions that a second order model, whilst a good basis for reaction, often only partially describes the processes occurring. In some recent work for example, Coughlin,[65] studying the uncatalysed reaction of TMXDI and Thompson,[66] investigating the formation of TDI-based prepolymers, were both unable to fit the kinetic data they obtained to any standard models.

1.6.6 Interest in Polyurethane Chemistry

Polyurethanes are industrially important for the manufacture of a wide variety of end products. These include tyres, automobile parts, shoe-soles, cable coatings, upholstery foams and insulating materials. Another area of increasing interest however is the development of polyurethanes for use as biomaterials.

A biomaterial is defined as any substance that is used in contact with living tissues and biological fluids for prosthetic, diagnostic or therapeutic applications, without adversely affecting the biological constituents of the entire living organism.[67] During the last 20 years, a number of medical-grade polyurethanes have been developed and used successfully. Some examples of biomedical urethane devices are listed overleaf.[68]

Total artificial hearts
Heart valves
Vascular prostheses
Pericardial patches
Roller pump tubings in artificial heart or blood pumps
Vascular stents
Intraaortic baloons
Mammary implants
Oesophageal and tracheal prostheses
Ureteral prostheses
Fallopian tubings
Endotracheal tubings
Gastric baloons and feeding tubings
Catheters and cannulas
Sutures, ligaments
Wound dressings and drapes
Blood bags
Peripheral nerve repair devices
Implants for craniofacial and maxillofacial reconstruction
Liners in dentistry and paradental membranes
Shock absorbing elements for root implants
Adhesives
Orthopedic casting tapes
Drug delivery devices
Enveloping membranes for soft organ fixation
Dialysis membranes
Filters in blood oxygenators
Meniscus reconsturction membranes
Endovascular embolization
Pacing leads insulation
Angioplasty baloons

Figure 1.17 Applications of Biomedical Polyurethanes

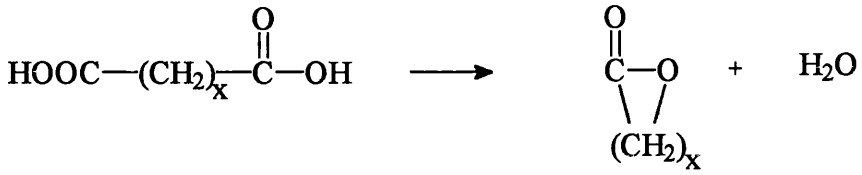
It is obviously important that biomaterials within the human body or in contact with the skin do not give rise to serious toxic or inflammatory responses. Additives such as plasticisers, catalysts and curing agents, together with any unreacted monomers or products of polymer degradation, all have the potential to leach from the polymer into body tissue.

The aim of current work is to investigate the effect of ultrasound on polyurethane synthesis. Ultrasound may have the potential to increase the rate of reaction and perhaps to reduce or eliminate the need for a catalyst, thereby resulting in a purer product. It may also enable accurate control over polymer molecular weight and polydispersity.

1.7 Polylactones

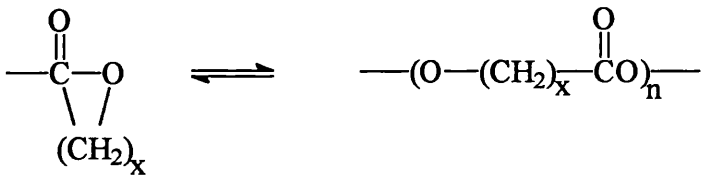
1.7.1 Basic Chemistry

Lactones are cyclic esters formed by the dehydration of hydroxy acids.



Four to seven membered rings are easily made by this method, but attempts to synthesise larger and smaller rings usually results in polyester formation, which is favoured over cyclisation.[69]

The ability of certain lactones to be ring-opened to high molecular weight compounds has been known for many years,[70] with Carothers[71] first identifying the process as a step-growth polymerisation.



Although a few lactones polymerise with great ease, apparently spontaneously on standing or heating,[72] most only do so under the influence of catalysts or initiators. The role of these species will be considered in the next section.

1.7.2 Formation of Polylactones

The ring-opening and subsequent polymerisation of lactones is usually performed by means of an initiator or catalyst. Although the term "catalyst" is used

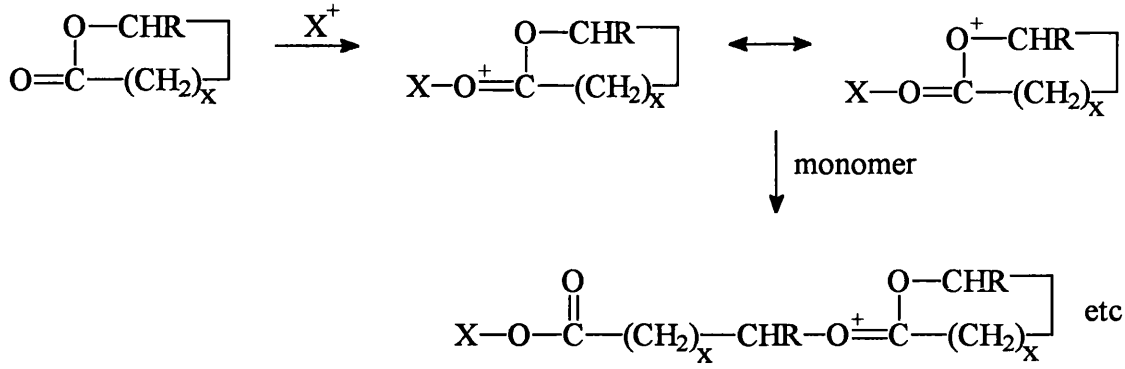
frequently in the field, it is often applied incorrectly as materials added in catalytic quantities often remain as end groups on the polymer chain and are not regenerated. The term should therefore be taken to mean a reaction component present in small quantities (1 wt. % or less), in addition to the initiator.

A number of species have been found to initiate lactone ring-opening: certain cations and anions; organic tertiary bases; alkali and alkaline earth metals, hydrides, alkoxides and alkyls; certain co-ordination complexes resulting from the reaction of alkylzinc or alkylaluminium compounds with alcohols or water; and hydrogen donors. The more widely used methods will be considered in turn.

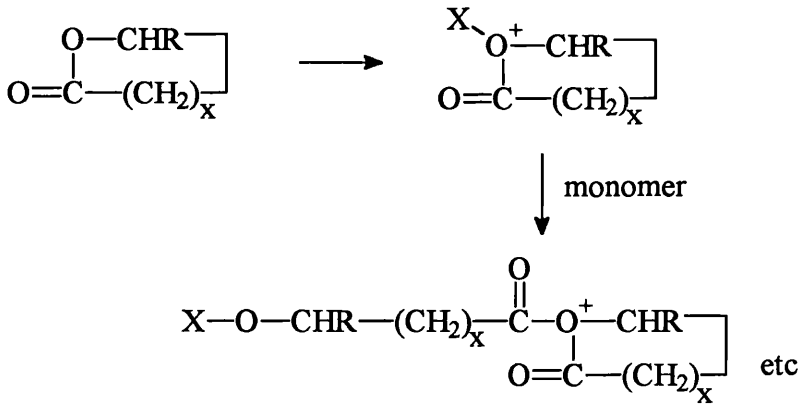
Cationic Ring-Opening

Strong protonic acids,[73] Lewis acids[74] and alkylating reagents[75] have all been used to effect the cationic ring-opening of lactones. Alkylating reagents such as methyl tosylate and methyl triflate have been found to be particularly useful as they yield stable end groups to polymer chains.[16]

Reaction occurs *via* two principal mechanisms.[4] The dominant mechanism for unsubstituted lactones (i.e. R = H), involves addition of X^+ to the carbonyl oxygen atom to form an oxonium ion, followed by scission of the O-CHR bond upon nucleophilic attack by another molecule of the monomer (see overleaf).

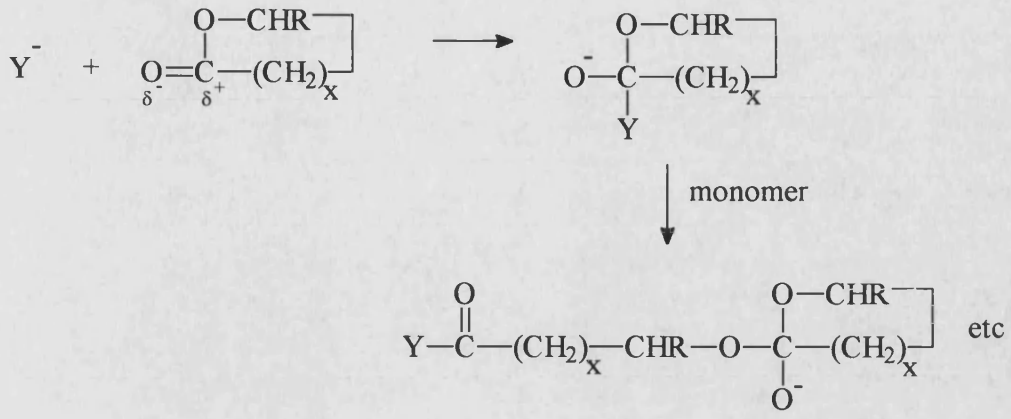


For substituted lactones (e.g. R = alkyl), the mechanism above would result in inversion of configuration of the asymmetric carbon atom CHR. The following mechanism is more probable due to the steric and inductive effects of the substituent, and involves retention of configuration of the asymmetric carbon atom. Initial addition of X^+ to the ring oxygen atom is followed by scission of the acyl-oxygen bond.



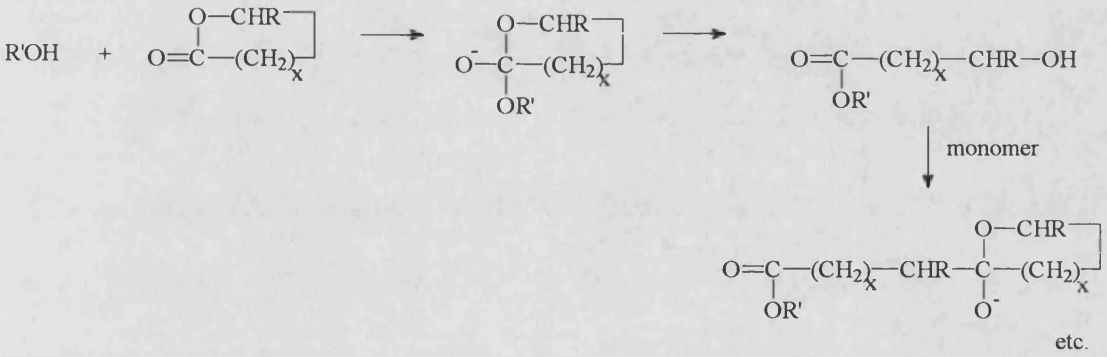
Anionic Ring-Opening

Anionic initiators for lactone ring-opening include alkali metals,[76] metal alkoxides[77] and inorganic bases.[73] Polymerisation occurs *via* attack at the carbonyl carbon of the monomer, followed by scission of the acyl-oxygen bond.



Hydrogen Donors

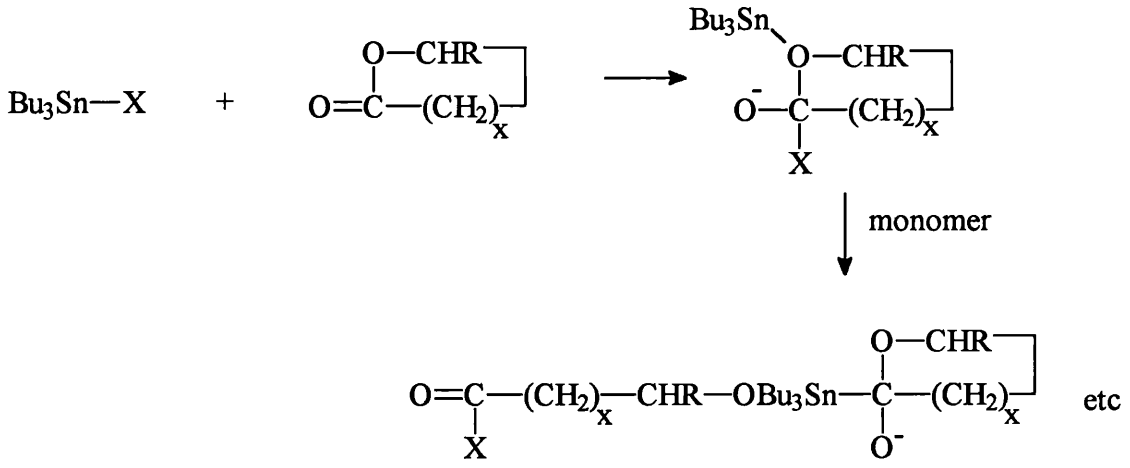
The use of hydrogen donors as initiators is widespread.[74] Examples include alcohols, glycols and amines. When hydroxyl compounds are used, reaction is by way of acyl-oxygen cleavage to give an intermediate ω-hydroxy ester.



Use of Tin Salts

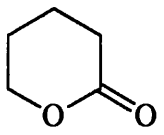
Tin salts are common catalysts/initiators for many types of polymerisation reaction and are often used to initiate lactone ring-opening.[53] Detailed studies of their reaction mechanism are lacking, but recent authors suggest that reaction is a result of acyl-oxygen scission.[78,79]

Kricheldorf[78] carried out experiments with tributyltin derivatives and using ^1H NMR detected only trace amounts of acetate end groups (resulting from alkyl-oxygen scission). This supported an acyl cleavage reaction as shown below:

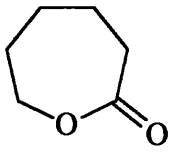


1.7.3 Ring-Opening of δ-Valerolactone and ε-Caprolactone

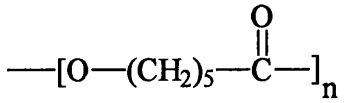
δ-valerolactone and ε-caprolactone are 6- and 7-membered lactone rings which are liquids at room temperature.



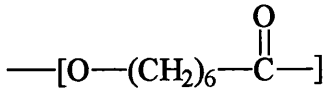
δ–valerolactone



ε-caprolactone



polyvalerolactone



polycaprolactone

A number of workers have studied their homo and copolymerisation. Carothers,[80] in the 1930's was one of the first to report polymerisation of δ-valerolactone in the presence of inorganic salts. Today, polymerisation of the monomer is common with a variety of initiator types.

Although readily polymerised, the ability of polyvalerolactone to undergo depolymerisation to the monomer at temperatures above 200°C was soon recognised.[80,81] Saotome[81] discovered that depolymerisation could be prevented by acylating the end hydroxyls of the polymer chains with acetic anhydride.

Polycaprolactone has been found to behave quite differently, remaining stable at high temperatures. Storey[82] suggested that the tendency for ε-caprolactone to form high molecular weight material under reaction conditions for which δ-valerolactone yielded little polymer, was a result of differing equilibrium monomer concentrations (M_e). In the case of ε-caprolactone, the monomer-polymer equilibrium during reaction is strongly in favour of the polymeric species.

A characteristic of certain anionic- and cationic-initiated δ-valerolactone and ε-caprolactone polymerisations is the ability to produce "living polymers" (i.e. polymers for which there is a total absence of any formal termination reactions and which consequently have very narrow polydispersities). Lundberg,[83] in 1969, polymerised ε-caprolactone using dibutyl zinc as a catalyst. He found that molecular weight and conversion increased simultaneously, indicative of a living system, and also that on adding more monomer to the system after apparent cessation of reaction, polymer of a higher molecular weight was obtained. Other workers have used alkali metals[84] and aluminium alkoxides[85] to similar effect.

1.7.4 Rates of Hydrogen-Donor Initiated δ-Valerolactone and ε-Caprolactone Polymerisation

The rates of reaction and molecular weights resulting from lactone ring-opening are highly dependent on the nature of the initiator (cationic, anionic, hydrogen-donor etc.) and on the reaction conditions employed.

In the current study, experiments were performed using 1,6-hexanediol, so consideration will be limited to reactions involving hydrogen-donating initiators.

Saotome[81] was the first to consider the kinetics of δ-valerolactone polymerisation. He performed experiments with monoethanol amine as initiator at a range of temperatures and obtained molecular weights by means of refractive index measurements. He assumed that each initiating molecule initiated the growth of one polymer chain and therefore the concentration of polymer chains in the system was a constant and equal to that of the initiator. The rate of polymerisation is therefore:

$$-\frac{d[M]}{dt} = k[P][M]$$

[P] = moles of polymer chains, equal to moles of initiator, [I]

[M] = moles of monomer

So, $\ln [M] = -k[I]t$

The number average molecular weight is:

$$M_n = \frac{W}{[P]+[M]}$$

where W is the total weight of the system.

By using this relationship between M_n and [M], Saotome was able to calculate [M] at different reaction times. Graphs of 1/ log [M] versus time were found to yield straight lines (i.e. second order reaction) and an Arrhenius plot of rate constants gave an activation energy of 26.8 kJ mol^{-1}.

More recently, Schindler[86] investigated the initiation of ε-caprolactone with 1,6-hexanediol, using stannous octoate as a catalyst. He found the reaction to be characterised by rapid initiation, with an invariance in the number of growing chains. With increasing conversion however, a broadening of molecular weight distribution occurred. Schindler speculated that this was due to ester interchange reactions, i.e. attack of polymeric ester functionalities by terminal hydroxyl groups of the polymer as the monomer was depleted. Such reactions are well documented in lactone ring-opening,[75] occurring particularly in ionically initiated systems.

Interestingly, Schindler found little polymerisation in ε-caprolactone that was "initiator free" and contained merely stannous octoate. He attributed the little polymerisation seen to residual water in the monomer. This is in contrast to work by Rafler,[79] who observed polymerisation in ε-caprolactone containing stannous octoate alone - indeed a high rate of conversion was achieved. Gorda[87] also used stannous octoate as a catalyst, this time in dioctyl amine initiated ε-caprolactone polymerisation. Increasing the amount of "catalyst" was effective in producing a higher degree of polymerisation. Gorda suggested that whilst initiation was almost spontaneous, the role of the catalyst was to promote the "propagation" stage of polymerisation i.e. the reaction of a hydroxy-terminated ring-opened monomer with another monomer molecule.

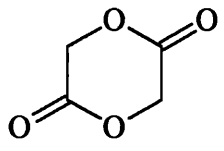
This difference in findings between various workers suggests that the role of catalysts and of tin salts in particular is still open to question.

1.7.5 Interest in Polylactones

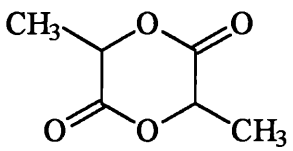
Block and graft copolymerisation of ε-caprolactone with numerous commercial polymers has led to many potentially useful materials. The ozone resistance of SBR elastomers for example, has been improved by copolymerisation,[88] whilst the incorporation of diblocks of ε-caprolactone into PVC have been found to markedly improve its properties for use in wire and cable insulation.[89]

Currently there is increasing interest in the use of biodegradable aliphatic polyesters, particularly in the fields of resorbable sutre materials and sustained release systems for drugs and agrochemicals.[79] The ability of their biodegradation products to be excreted in human metabolic processes, makes them especially important.

High molecular weight products of these polyesters are formed by the ring-opening of cyclic esters like lactones and glycolides. Glycolide and its dimethyl derivative, lactide are shown below.



glycolide



lactide

The high crystallinity and low hydrophobicity of polylactide and polyglycolide polymers can worsen their drug permeability and compatibility with soft tissue.[77] These

problems are overcome by block copolymerisation with ε-caprolactone, which possesses good permeability and compatibility.[90]

Other workers have investigated the copolymerisation of δ-valerolactone and ε-caprolactone as potentially useful biomaterials.[82,91]

In conclusion, the study of polylactones and in particular their physical properties and stability is an area of great interest. Ultrasound may play a role in controlling polymer weights as well as in increasing reaction times and removing the need for initiators and/or catalysts.

1.8 Program of Work

To investigate the use of ultrasound in polyurethane formation, a number of isocyanate-diol reactions were carried out. One particular system, that of H_{12}MDI and 1,4-butanediol, was studied more thoroughly with measurements of polymer molecular weight and a study of the effects of ultrasonic intensity. Kinetic measurements were also performed using a variety of analytical techniques.

Polylactone experiments concentrated on the ring-opening of δ-valerolactone and ε-caprolactone. The relationship beween polymer molecular weight and sonication time were studied at a variety of ultrasonic intensities and reactions were also performed in solution. Copolymers of the two lactones were synthesised and their composition studied by means of DSC and ^{1}H NMR.

CHAPTER TWO

EXPERIMENTAL

CHAPTER 2

2.1 Materials

The following diisocyanates were used in polymerisation experiments; 4,4-dicyclohexylmethane diisocyanate (H_{12}MDI), Bayer, isophorone diisocyanate (IPDI), Hüls, 1,3-bis (1-isocyanato-1-methylethyl)-benzene (m-TMXDI), Bayer, Suprasec VM10 (modified pure MDI [4,4-diphenylmethane diisocyante]), ICI and Desmodur Z, Bayer.

The OH-containing compounds used in the same experiments were all obtained from Aldrich Ltd; 1-propanol (HPLC Grade, 99.5%), 1-butanol (HPLC Grade, 99.9%), 1,4-butanediol (99%), poly(ethylene glycol), average molecular weight 300, and poly(ethylene glycol), average molecular weight 600.

For the study involving H_{12}MDI detailed in Section 3.2, additional materials were used, ethylene glycol (99.8%), diethylene glycol (99%), triethylene glycol (99%), tetraethylene glycol (99%), poly(ethylene glycol), average molecular weight 200, and poly(ethylene glycol), average molecular weight 400. All were from Aldrich Ltd. The water content of these compounds was measured using the Karl Fischer method[92] and is detailed in Appendix 1.

Dibutyltin dilaurate (98%), Aldrich Ltd, was the catalyst for the polyurethane experiments; sometimes as a solution in 2-butanone, HPLC Grade (99.9%), Aldrich Ltd. and sometimes "neat".

The back titration study, Section 3.3.2, required the use of dibutylamine (99+%), toluene (HPLC grade, 99.8%), 2-propanol (HPLC grade, 99.5%) and

bromophenol blue (0.1% solution in 1.5 x 10^{-5} mol dm^{-3} NaOH). All were from Aldrich Ltd.

Heptane (HPLC grade, 99+%), tetrahydrofuran (HPLC grade, 99.9%) and tetradecane (99+%), once more from Aldrich Ltd, were used in gas chromatography experiments. Gases for chromatography; air, hydrogen and nitrogen were supplied by BOC Ltd.

The monomers used for lactone ring-opening polymerisations were δ-valerolactone (99%), Lancaster, and ε-caprolactone (99+%), Aldrich Ltd. These were initiated with 1,6-hexanediol (99+%) and catalysed with dibutyltin dilaurate (98%), both from Aldrich Ltd. Solution experiments were performed in butyl benzoate (99%), Aldrich Ltd. Resultant polymers were purified using dichloromethane (S.L.R.) and hexane (A.C.S. reagent), again from Aldrich Ltd.

GPC analysis was performed on polylactone samples using tetrahydrofuran (HPLC grade 99+%) as both solvent and eluent.

$CDCl_3$ (99.8% containing 0.03% v/v TMS), Aldrich Ltd. was used as an NMR solvent for polyvalerolactone and polycaprolactone samples.

2.1.1 Safety Considerations

Diisocyantes pose a particular risk to health and great care is needed when handling them. The principal hazard arises from vapour and therefore the degree of hazard depends on the vapour pressure of the particular isocyante. Exposure to vapour has been found to irritate the membrane of the nose, throat, lungs and eyes.

Additionally, aliphatic diisocyantes can have adverse skin irritation effects. $H_{12}MDI$ (used in this study) is particularly prone to produce such a reaction.

Diisocyantes were therefore handled exclusively in high toxicity fume cupboards and rubber gloves were worn at all times. To clean contaminated glassware and to deal with any spillages, a neutralising solution was prepared, comprising;[93]

Alcohol (ethanol/isopropanol)	50%
Water	45%
Conc. Ammonia Solution	5%

Details of the hazards arising from specific diisocyanates are described in Appendix 2.

2.2 Sonication Experiments

2.2.1 Ultrasonic Equipment

The majority of experiments in this study used ultrasonic probes in preference to baths, as a much greater ultrasound intensity was obtained. Three different probes were used for different areas of work. Selection of the probe depended on such criteria as the volume of reactants used, the physical dimensions of the probe in relation to the reaction vessel and the ultrasonic power available. The three probes were;

a) VC 50, Sonics and Materials Ltd., power 18.4-27.0 Wcm^{-2}, horn 6 mm in diameter, 20 kHz.

b) Soniprep 150, Curtin Matheson Sci. Ltd., power 17.6-30.6 Wcm^{-2}, horn 9.8 mm in diameter, 23 kHz.

c) VC 600, Sonics and Materials Ltd., power 20.3-40.4 Wcm^{-2}, horn 12 mm in diameter, 20 kHz .

The probes were calibrated as described in section 2.2.2. A Ney "Ultrasonik" 300 Bath was also used in several preliminary experiments.

2.2.2 Calibration of Probes

There are various methods of stating the ultrasonic power used during sonication. Some workers report the nominal output as described by the equipment manufacturers. This has the disadvantage that the manufacturer's value is normally related to the amount of energy being supplied to the transducer and bears no relationship to the amount of energy being transferred to the reaction.

An alternative approach is to use a calorimetric method, whereby a value is stated for the time taken to heat a known volume of distilled water through a measured temperature rise. The heat capacity of the reaction vessel is taken into account in such a method, so other workers using different types of vessel should be able to make a direct comparison with the results obtained.

The calorimetric method and calculations are described below for the three probes used.

Calorimetric Method

To calibrate the VC 600 probe, a jacketed glass vessel was set up as for a sonication experiment, see Section 2.2.3, but an electric heater and a thermocouple were inserted. After pipetting 50 cm^3 of distilled water into the vessel, the system was allowed to equilibrate to room temperature and the initial temperature was noted. The

heater was then switched on and the voltage and current passing through it were recorded using a multimeter. Temperature readings were taken at regular intervals. On completion, the heater was removed and the experiment was repeated with a fresh volume of water using the ultrasonic probe as the heat source. The temperature was monitored over the same time period as before. The heating effects of five generator settings were investigated; 3, 4, 5, 6, and 7. Results are illustrated graphically in Figure 2.1.

Calculation

Examination of Figure 2.1 shows that the temperature rise was initially rapid, but with time became progressively slower. For calculation purposes the rise is only considered over the range 0-120 s. It is in this region that the effect of the different intensity settings on the heating rate is most marked.

The energy E, supplied by the heater is calculated as shown below:

Current I = 1.139 A Voltage V = 15.51 V

$E = VIt$

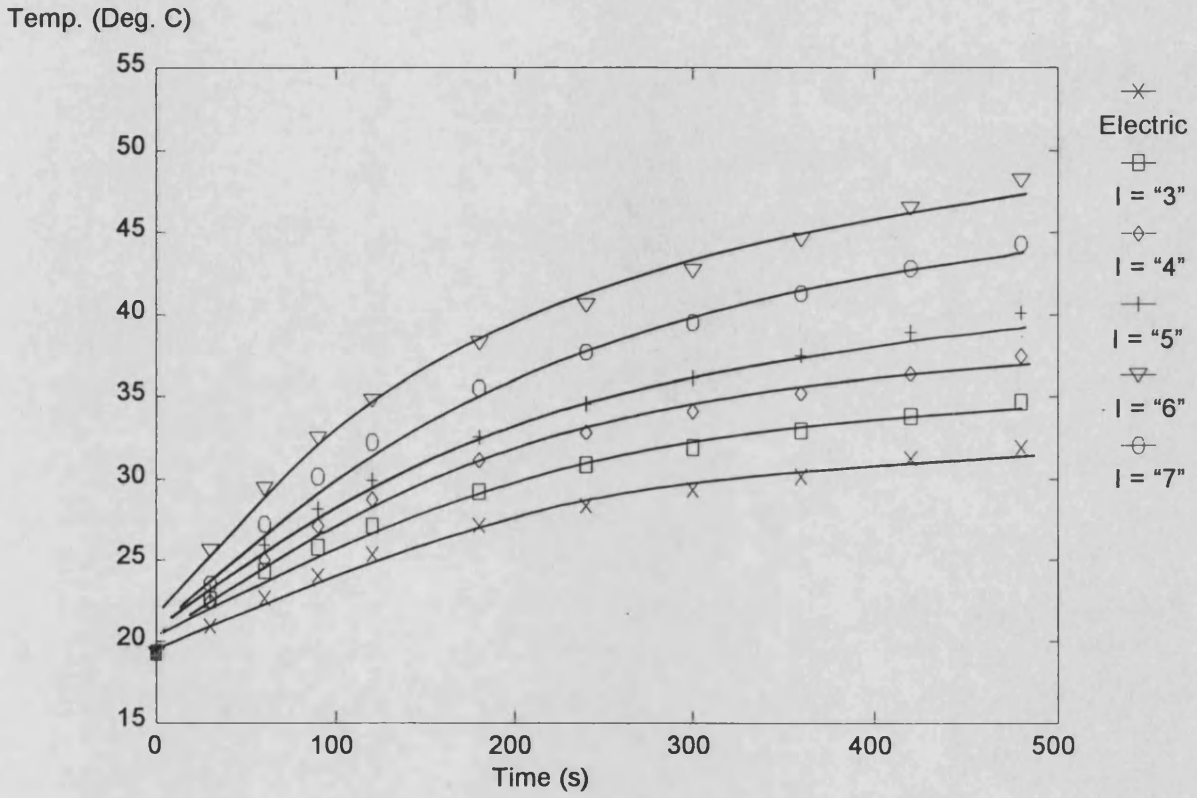
$E = 2119.9$ J

The total heat capacity of the system (including the water, reaction vessel, probe etc.) can be assumed to be a constant for the experiments and is given the term C. If heat losses to the surroundings are ignored, then the energy supplied by the heater is equal to the energy gained by the system:

$E = C\delta\theta$

Figure 2.1

Calibration of VC 600 Probe:
Variation of Temperature with Time at different Ultrasonic Intensities



In the period 0-120 s a temperature rise $\Delta\theta$ of 6.0°C was observed, therefore:

$\underline{C = 353.3\ JK^{-1}}$

Now that the value of C is known, the power of the probe may be calculated for each of the settings under investigation, using the relationship below:

Power = VI So, $Pt = E = C\Delta\theta$

$P = C\ \Delta\theta/t$

$\Delta\theta/t$ for the range 0-120 s is listed for each intensity, together with the value of the power obtained:

Setting:	3	$\Delta\theta/t = 0.0065$	**P** = 22.96 W
	4	$\Delta\theta/t = 0.0783$	**P** = 27.66 W
	5	$\Delta\theta/t = 0.0883$	**P** = 31.20 W
	6	$\Delta\theta/t = 0.1075$	**P** = 37.98 W
	7	$\Delta\theta/t = 0.1292$	**P** = 45.65 W

When quoting ultrasound intensities, the area of the probe tip must be taken into account.

Diameter probe tip = 1.2 cm

Area probe tip = $\pi\ (1.2/2)^2 = 1.13\ cm^2$

Resultant intensity values are therefore as follows:

Generator Setting	Intensity (Wcm^{-2})
3	20.3
4	24.5
5	27.6
6	33.6
7	40.4

Estimation of Uncertainties

It is not possible to quantify all errors in the experiment, e.g. those arising from non-efficient heat transfer and inevitable heat losses to the surroundings. Errors resulting from temperature measurement and timing may be estimated however.

Error in thermocouple reading = $\pm$ 0.1°C

$\Delta\theta$ for electric heating = $T_2 - T_1$

So error = $\pm$ [0.1/25.3 + 0.1/19.3] x 100% = $\pm$ 0.91%

Considering $\Delta\theta$ for ultrasound (e.g. I = 5)

Error = $\pm$ [0.1/29.9 + 0.1/19.3] x 100% = $\pm$ 0.85%

Hence, total error in temperature readings = $\pm$ 1.76%

Error in stopclock reading = ± 1s

i.e. error in timing of electric and ultrasonic heating is:

error = ± [1/120 + 1/120] x 100% = ± 1.67%

Hence, total error for heating and timing combined is approximately 3.4%. Strictly speaking, intensities should be quoted with this error, for example for setting 5:

$I = (27.6 \pm 0.9)\ Wcm^{-2}$

Calibration of other Probes

Calibration of the Soniprep 150 generator was carried out in an identical manner, but with a 25 cm^3 volume of water. Results are illustrated in Figure 2.2. Intensities were calculated as outlined previously and the powers are listed below:

Generator Setting	Intensity (Wcm^{-2})
8	17.6 (± 0.6)
10	20.1 (± 0.7)
14	28.5 (± 1.0)
18	30.6 (± 1.0)

The calibration of the VC 50 probe was performed in a beaker rather than a jacketed vessel, to more closely mimic lactone polymerisation experiments. Results are illustrated in Figure 2.3 and intensities listed below.

Figure 2.2

Calibration of Soniprep 150 Probe:
Variation of Temperature with Time at different Ultrasonic Intensities

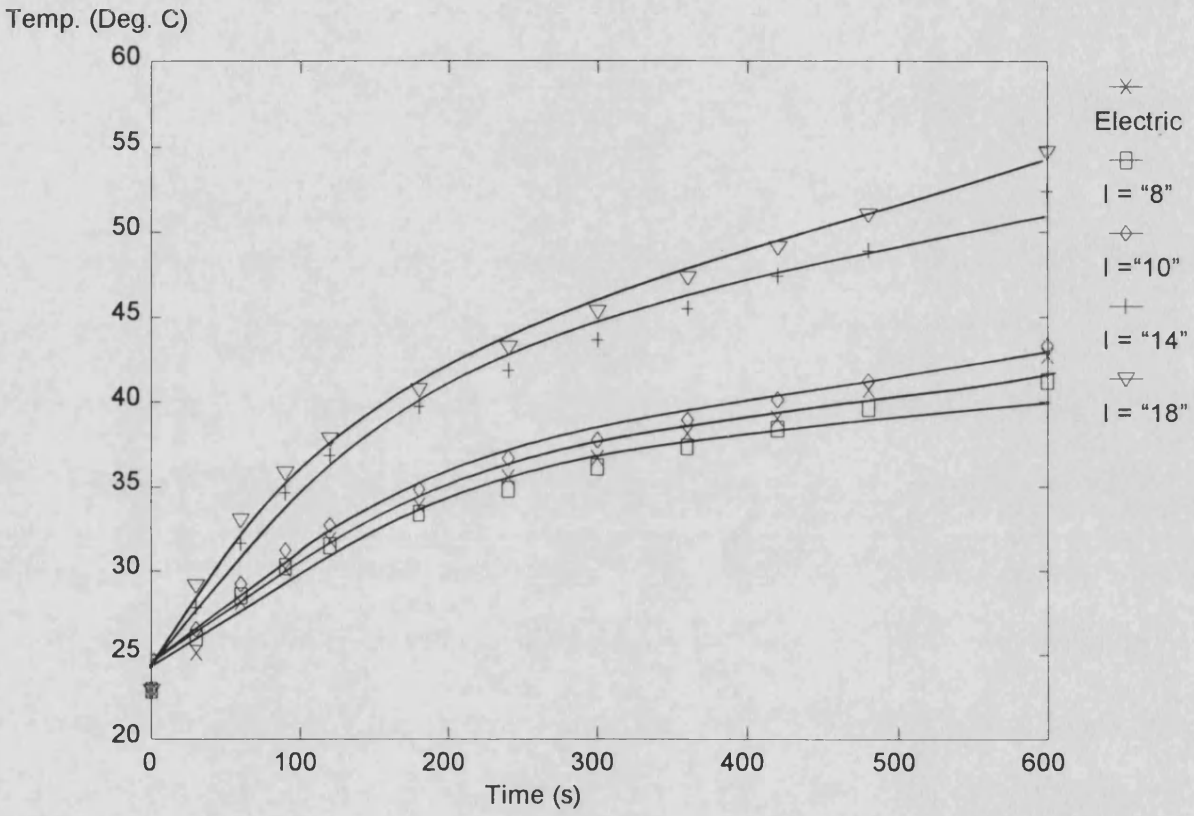
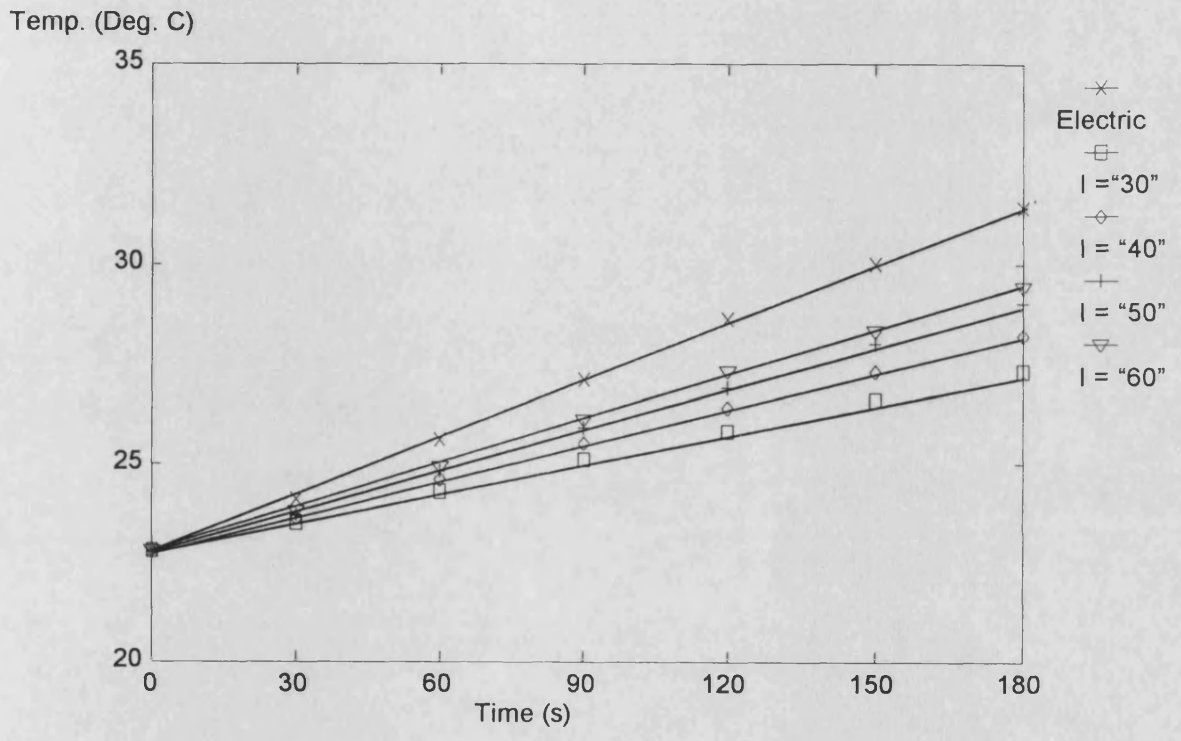


Figure 2.3

Calibration of VC 50 Probe
Variation of Temperature with Time at different Ultrasound Intensities



Generator Setting	Intensity (Wcm^{-2})
30	18.4 (± 0.6)
40	22.1 (± 0.8)
50	25.4 (± 0.9)
60	27.0 (± 0.9)

2.2.3 Polyurethane Production

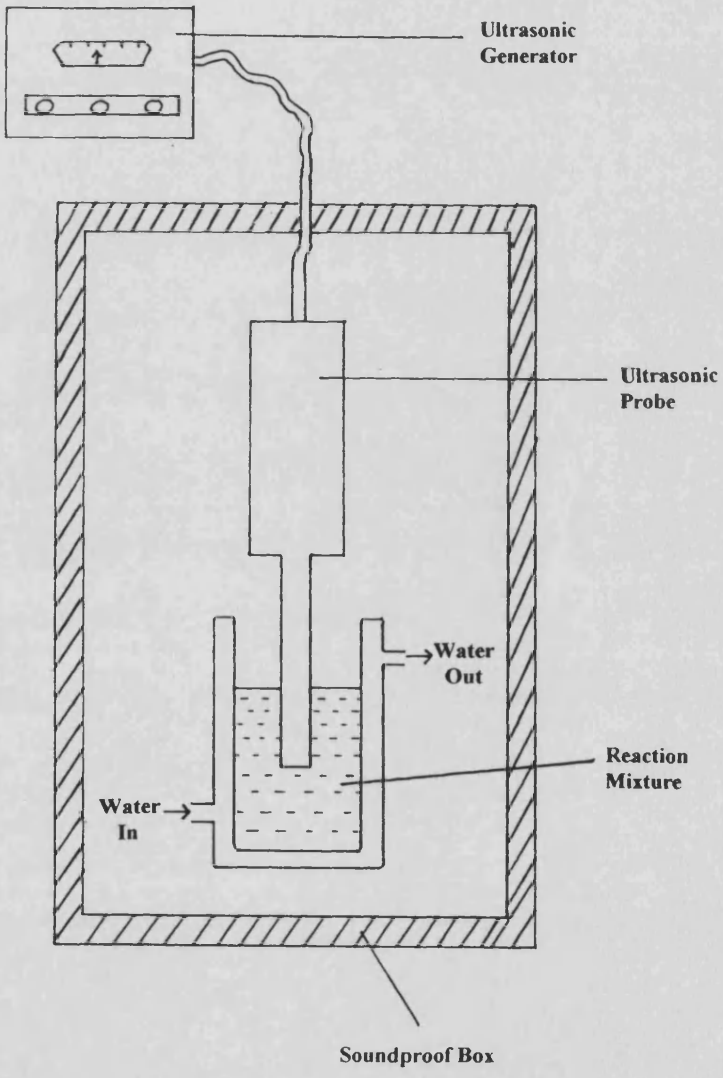
The first set of experiments (Section 3.1), involved a comparison of ultrasonic, thermal and stirred polyurethane production with a wide range of monomers.

To perform the sonication experiments, a beaker-shaped jacketed glass vessel (maximum capacity 50 cm^3) was used to contain the reactants and the Soniprep 150 probe was inserted into it. By circulating water through the jacket, temperature rises were kept to a minimum. A thermocouple was used to monitor the temperature of the reaction mixture. The experimental set up is shown schematically in Figure 2.4.

The monomers (diisocyante and OH-containing compound) were reacted in a 1:1 molar ratio and 0.1% by weight of dibutyltin dilaurate catalyst was added in some experiments. The catalyst was present as a 1% solution in 2-butanone in order to enable weighing to be performed accurately. The total volume of reactants was usually in the range 10-30 cm^3.

Figure 2.4

Ultrasonic Polymerisation Apparatus



Experiments in the ultrasonic bath were performed by clamping a small bottle containing the reactants (~3.5 cm^3) at a point of maximum agitation within the water.

The extent of polymerisation in all sonications was determined visually (i.e. by observing the increasing viscosity of the reaction mixture and the ultimate formation of a solid). The end of the reaction (solid formation) could be pinpointed accurately by a sudden change in ultrasonic pitch, as resistance to wave propagation through the mixture increased. It was necessary to remove the probe from the reaction vessel at this point to prevent it becoming encased in polymer.

Control experiments were carried out in an oven at 50°C and 80°C. Reactants were contained in sample bottles and inspected at regular intervals. Several stirred reactions were also performed, using a magnetic stirrer.

A further study investigated the reaction of H_{12}MDI with a series of ethylene glycols (Section 3.2). The VC 600 probe was selected for this work. It offered greater ultrasonic power than the Soniprep 150 and, as not incorporated into a soundproof box, enabled easier manipulation and speedier withdrawal of the probe from the reaction mixture on completion of polymerisation.

As before, reactions were carried out in a water jacketed vessel with a thermocouple to monitor temperature rise. A 1:1 molar ratio of diisocyante and OH-containing compound was used and dibutyltin dilaurate was either added neat (3 drops, ~0.04 g) or as a 1% solution in acetone to give the equivalent of 0.1% by weight of catalyst. The total volume of reactants was in the range 32.5 cm^3 - 37.5 cm^3. Stirred reactions were performed as a control on the same volume of reactants.

2.2.4 Production of Polyvalerolactones and Polycaprolactones

A VC 50 probe was used throughout the polylactone study. It had the lowest power of the three probes available and therefore produced the smallest heating effect. This was important, as only small volumes of reactants were used in each experiment.

In a typical experiment, 15 g of monomer (valerolactone or caprolactone) was reacted in a 30:1 ratio with the initiator, 1,6-hexanediol (the reason for the selection of this ratio is discussed in Section 4.1). Approximately 1% by weight of dibutyltin dilaurate catalyst was added to the mixture. Sonications were performed in a beaker clamped in an oil bath. The temperature of the oil bath was kept constant by means of a thermostatted heater-stirrer and temperature within the reaction mixture was monitored regularly with a thermocouple. The thermostat of the stirrer was adjusted to maintain an approximately constant reaction temperature (± 4°C). Reactions were performed at either 150°C or 170°C.

In order to follow the polymerisation, samples of the reaction mixture (~0.2 cm^3) were taken at regular intervals and immediately quenched in liquid nitrogen to prevent further reaction. Each sample was then dissolved in 5 cm^3 of dichloromethane and reprecipitated with vigorous stirring from a ten-fold excess of hexane. The resultant polymer was washed three times with hexane and dried in a vacuum oven at 80°C for 6 hours. Samples were analysed by gel permeation chromatography (Section 2.3.1).

Thermal experiments were performed in an identical manner, with reactants being placed in a beaker in an oil bath and stirred at a constant temperature.

2.3 Polymer Analysis

2.3.1 Molecular Weight Measurement using Gel Permeation Chromatography

a) Polyurethanes

Polyurethane samples were analysed by GPC at RAPRA Technology Ltd. Sample solutions were prepared by adding 10cm^3 of dimethylformamide to 20 mg of sample and leaving overnight to dissolve. On the following day, solutions were gently warmed for 20 minutes and a small amount of 1,2-dichlorobenzene was added as an internal marker for flow-rate calibration purposes. The solutions were then thoroughly mixed and filtered through a 0.2 μm PTFE membrane.

The chromatograph contained two 30 cm PLGel mixed bed columns and the eluting solvent was DMF to which LiBr had been added to prevent the possible occurrence of non-steric effects. Samples were run at a flow rate of 1.0 cm^3 min^{-1} and at a temperature of 80°C. Analysis was carried out with a refractive index detector and the system was calibrated with poly(ethylene oxide) and poly(ethylene glycol) standards, resulting in molecular masses expressed as "PEO/PEG equivalents".

b) Polyvalerolactones and Polycaprolactones

A Bruker LC41 system fitted with a 60 cm Polymer Laboratories Ltd. PLGel Mixed Bed columns was used to analyse polylactone samples. The samples were prepared as 0.5% w/v solutions in tetrahydrofuran and each was filtered through a 0.2 μm Nylaflo filter before injection. The eluent (THF) was pumped at 1.0 cm^3 min^{-1} at room temperature and analysis was carried out with a refractive index detector.

Calibration of the system was undertaken using low polydispersity polystyrene standards supplied by Polymer Laboratories Ltd. The molecular weights of the standards were 1030000, 675000, 127000, 68000, 30300, and 9200.

2.3.2 GPC Viscometry

GPC viscometry was performed on selected polyvalerolactone and polycaprolactone samples at RAPRA Technology Ltd. Sample solutions were prepared by adding 7 cm^3 of THF to 20 mg of sample and leaving overnight to dissolve. A small amount of 1,2-dichlorobenzene was added to act as an internal marker and the solutions were accurately made up to 10 cm^3. Filtering took place through a 0.2 μm polyamide membrane prior to injection.

Chromatography was performed with two PLGel mixed bed-B columns, 30 cm in length. The eluent was THF, flowing at a rate of 1.0 cm^3 min^{-1} at room temperature. Results were computed using the outputs from both a viscosity and refractive index detector.

2.3.3. Infrared Spectroscopy

Infrared spectroscopy was used to monitor several diisocyante-alcohol reactions. Monomers were reacted in a 1:1 molar ratio with a total reaction volume of 15-20 cm^3. Where a solvent was used (THF), this accounted for 50% of the volume. Solutions were either sonicated in a water jacketed vessel with a Soniprep 150 probe or stirred with a magnetic stirrer. Samples were removed periodically and infrared spectra were run as liquid films on NaCl plates, using a Perkin Elmer 983 Spectrophotometer.

2.3.4 Gas Chromatography

Packed Column

A very short study was performed using a packed column gas chromatograph. Measurements were carried out on a Pye Unicam GCD with a flame ionisation detector, and processed using a Hewlett Packard 3394 integrator. The column material was 3% OV1 on Chromosorb WHP, 100/120 mesh.

Typical analysis conditions were:

Air: 8-9psi

H_2: 13psi

N_2: 15psi

Column temperature: 235-240°C

Capillary Column

Further work was performed using a capillary column to effect better separation. As before, a flame ionisation detector and Hewlett Packard 3394 integrator were used. Typical analysis conditions were as follows:

Air: 18psi

H_2: 27psi

N_2: 20psi

Column Temperature: 170°C

Detector Temperature: 270°C

2.3.5 Dibutylamine Titration

The dibutylamine back-titration is a standard method for determining the isocyanate content of a reaction mixture.[53]

The procedure involves the addition of an accurately known excess of dibutylamine to a sample taken from the reaction mixture. The NH group of the dibutylamine combines readily with any unreacted isocyanate in the sample. By titrating the remaining dibutylamine with acid, it is possible to calculate the amount of amine reacting with isocyanate and hence the percentage of isocyanate in the sample.

The kinetics of the reaction between IPDI and butanediol were investigated using an ASTM analytical method.[94] The monomers were reacted in a 1:1 molar ratio in a jacketed glass vessel, giving a typical volume of 20 cm^3. Sonications were performed with the Soniprep 150 probe.

At regular intervals, samples of approximately 0.1 g were taken and weighed accurately into a conical flask to which 2.5 cm^3 of dry toluene was added. Next, 2.5 cm^3 of 0.1M dibutylamine in toluene was added and the mixture was stirred for 15 minutes with a magnetic stirrer. 10 cm^3 of propan-2-ol was then added, together with 5 drops of bromophenol blue indicator. The mixture was titrated with 0.1M HCl to a yellow end-point.

A blank titration was also run, including all reagents except the reaction mixture sample.

The % NCO for each sample was calculated as follows:

$$\% \text{ NCO} = \frac{(B-V) \times M \times 0.0420}{W} \times 100\%$$

B = volume of acid for blank titration

V = volume of acid for sample titration

M = molarity of acid

W = mass of sample

A slightly different procedure was followed for the study involving the reaction between H_{12}MDI and butanediol.[95] DMF replaced toluene as the sample solvent as it gave much better solubility of the H_{12}MDI polymer.

5 cm^3 of 0.5M dibutylamine in DMF and 10 cm^3 of DMF were added to accurately weighed reaction samples. After 10 minutes of stirring, one drop of bromocresol green in water was added and titration was performed with 0.1M HCl to a yellow end-point.

2.3.6 NMR Analysis of Polymers and Copolymers

^{1}H NMR spectra of the homo and copolymers of polyvalerolactone and polycaprolactone were recorded on a Joel GX400 spectrometer. Samples were analysed as solutions in $CDCl_3$, with TMS as an internal standard.

2.3.7 Differential Scanning Calorimetry of Polymers and Copolymers

The melting points of homo and copolymers of polyvalerolactone and polycaprolactone were investigated using differential scanning calorimetry. A Dupont

910 module was used to carry out the measurements and results were analysed on a Dupont 9900 system. Indium and water were used as calibration standards.

CHAPTER THREE

ULTRASONIC POLYURETHANE FORMATION

CHAPTER THREE

The aim of this study was to investigate the effect of ultrasound on polyurethane formation. Of particular interest were differences between ultrasonic and conventional polymerisations, for example in reaction time or in the nature of the product. It is these factors which are of importance when producing commercial materials.

3.1 Initial Investigation of a Variety of Monomers

As the application of ultrasound to polyurethane reactions is a new area of research, initial work investigated a range of systems in order to obtain an understanding of general effects and to identify suitable monomers for further study. Results are classified according to the diisocyanate used in the reaction.

3.1.1. H_{12}MDI-Based Polyurethanes

H_{12}MDI is an aliphatic diisocyanate which is used in the manufacture of non-discolouring urethane coatings[96] (for structure see Section 1.6.3).

It was reacted with 1,4-butanediol, both with and without catalyst (dibutyltin dilaurate), using an ultrasonic bath, an ultrasonic probe and an oven. Table 3.1 shows results for the differing reaction conditions. Figure 3.1 illustrates the variations in ultrasonic and thermal polymerisation times for catalysed reactions whilst Figure 3.2 gives the same information for uncatalysed experiments. As described in Section 2.2.3, "polymerisation time" was the time taken for solid polymer to form.

Table 3.1

Polymerisation of H_{12}MDI with 1,4-Butanediol

Oven or Probe	Catalyst Present	Polymerisation Time	Comments
Oven: 50°C	0.2 wt. %	33 min	Hard, colourless polymer
Oven: 80°C	0.2 wt. %	20 min	Hard, colourless polymer
Probe: 20.1 Wcm^{-2}	0.2 wt. %	1 min	White, rigid foam
Ultrasonic Bath	0.2 wt. %	15 min	Hard, colourless polymer Av. temp. during son. - 26°C
Oven: 80°C	-	10 hr	Hard, colourless polymer
Probe: 17.6 Wcm^{-2}	-	5 hr	Hard, colourless polymer
Probe: 30.6 Wcm^{-2}	-	3 hr	Hard, colourless polymer Av. temp. during son. - 50°C

Figure 3.1

Comparison of Polymerisation Techniques for the Catalysed Reaction Between H_{12}MDI and 1,4-Butanediol

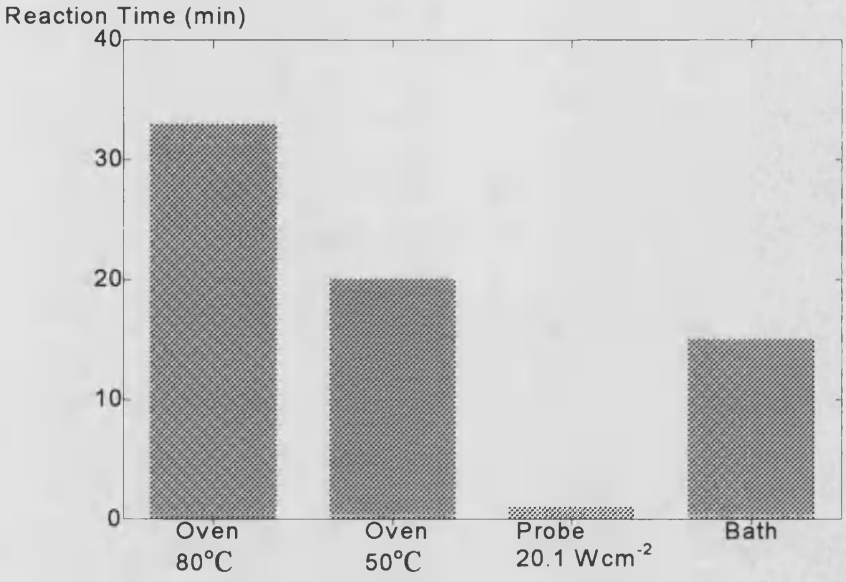
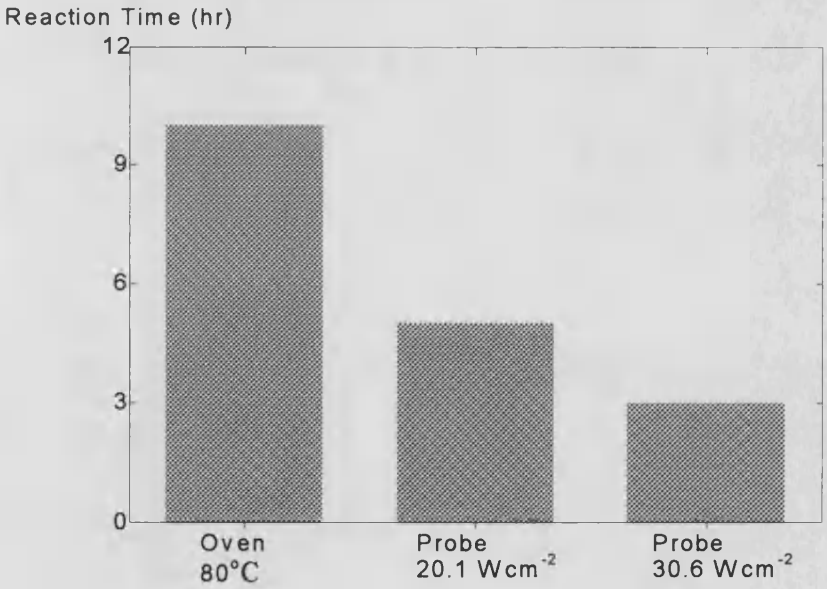


Figure 3.2

Comparison of Polymerisation Techniques for the Uncatalysed Reaction Between H_{12}MDI and 1,4-Butanediol



Several conclusions can be drawn from these preliminary results. Firstly, polyurethane formation took place much more rapidly in the presence of catalyst. Secondly, ultrasound was effective at promoting the polymerisation, giving much shorter reaction times than thermal experiments. This was particularly noticeable when sonicating a catalysed solution, which resulted in almost immediate production of a rigid foam. The foam was very different in appearance from the product of the thermal reaction. Foams normally only result when water is present in the reaction mixture (as discussed in Section 1.6.2). However, the butanediol used had a water content of just 0.23% and in any case, foaming was not observed in thermal reactions. It could be that the degassing effect of ultrasound gave rise to bubbles of gas or vapour which were trapped in the polymer structure.

The results obtained using an ultrasonic bath also illustrate the enhanced nature of the sonicated reaction. A solid product was obtained in about 15 minutes at a temperature of 26°C (as monitored with a thermocouple) whilst in an oven at 80°C, an identical volume of reactant required 20 minutes to polymerise to a similar degree.

Similarly, for an uncatalysed reaction, use of a probe resulted in polymer after 3 hours (average temperature 50°C). At least 10 hours were needed in an oven at 80°C.

3.1.2 VM10-Based Polyurethanes

VM10 is a commercial aromatic diisocyanate, composed of a mixture of MDI and TDI dimers (for structure of MDI and TDI, see Section 1.6.3). It is used in the manufacture of items such as shoe soles and flexible coatings.[53]

The results in Table 3.2 were obtained from reaction with several diols/glycols; 1,4-butanediol (BD), poly(ethylene glycol) RMM=300 (PEG 300), and poly(ethylene glycol) RMM-600 (PEG 600). It can be seen that production of polymer occurred readily without catalyst (in contrast to H_{12}MDI experiments). Figure 3.3 illustrates reaction times for experiments involving butanediol.

The use of a probe resulted in the rapid formation of a foam, whilst thermal experiments required longer reaction times and resulted in a polymer of a different appearance. Stirring however gave rise to a foam in about 10 minutes. This suggests that the efficient mixing effects produced in sonicated solutions aided polyurethane formation.

A similar pattern was observed on reaction of VM10 with PEG 300 and PEG 600. Sonication led to almost immediate polymer production, whilst heating the monomers took longer. Stirring gave reasonably quick formation of a viscous prepolymer, but this only cured with time.

3.1.3 TMXDI-Based Polyurethanes

TMXDI is an aliphatic diisocyanate (for structure see Section 1.6.3). Results of reaction with 1,4-butanediol are given in Table 3.3 and illustrated in Figure 3.4.

Once again, sonication gave significantly faster polymer production than heating or stirring. There was no difference in appearance however between the polymers produced by the three different methods. Gel permeation chromatographs were recorded of the polymer samples and results are given below. The molecular weights are relative to polystyrene calibration standards.

Table 3.2

Polymerisation of VM10 with 1,4-Butanediol, PEG 300 and PEG 600

Oven, Probe or Stir	Diol or Polyol	Catalyst Present	Polymerisation Time	Comments
Probe: 20.1 Wcm^{-2}	BD	0.05 wt.%	3 min	Brittle polymer
Probe: 20.1 Wcm^{-2}	BD	-	1 min	Brittle foam
Oven: 80°C	BD	-	30 min	Brittle polymer
Oven: 50°C	BD	-	1 hr	Brittle polymer
Stir	BD	-	10 min	Brittle foam
Probe: 20.1 Wcm^{-2}	PEG 300	-	1 min	Soft, sticky polymer becomes brittle when sonication stops
Oven: 80°C	PEG 300	-	55 min	Hard Polymer
Oven: 50°C	PEG 300	-	2hr	Hard Polymer
Stir	PEG 300	-	(9 min)	After 9 min too viscous to stir. Only hardens on being left over night
Probe: 20.1 Wcm^{-2}	PEG 600	-	1 min	Colourless polymer, slightly "tacky"
Oven: 80°C	PEG 600	-	25 min	Hard, colourless polymer
Stir	PEG 600	-	(20 min)	After 20 min too viscous to stir. Only hardens on being left over night

Figure 3.3

Comparison of Polymerisation Techniques for the Uncatalysed Reaction Between VM10 and 1,4-Butanediol

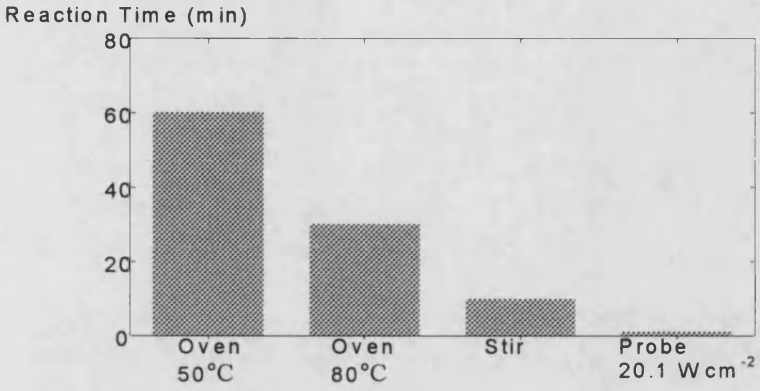


Figure 3.4

Comparison of Polymerisation Techniques for the Catalysed Reaction Between TMXDI and 1,4-Butanediol

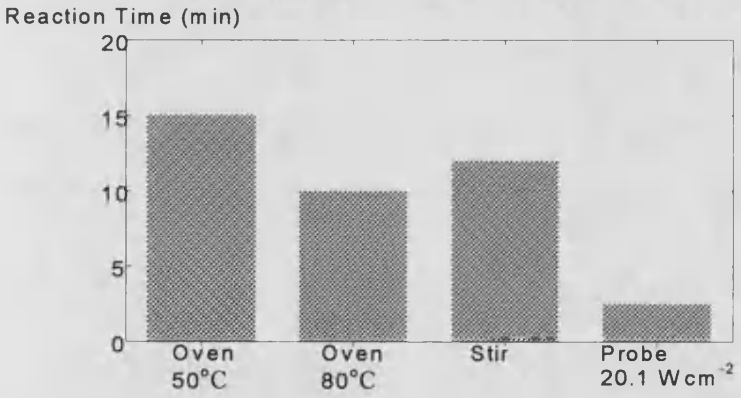


Figure 3.5

Comparison of Polymerisation Techniques for the Catalysed Reaction Between IPDI and 1,4-Butanediol

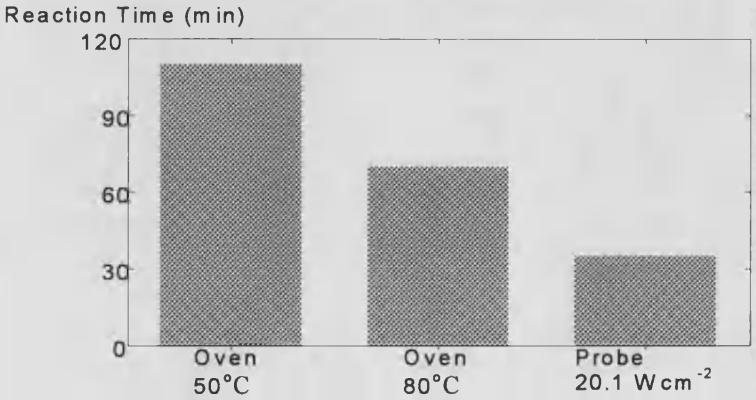


Table 3.3

Polymerisation of TMXDI with 1,4-Butanediol

Oven, Probe or Stir	Catalyst Present	Polymerisation Time	Comment
Probe: 20.1 Wcm^{-2}	0.01 wt. %	2.5 min	Hard, colourless polymer Av. temp. during son.- 50°C
Oven: 80°C	0.01 wt. %	10 min	Hard, colourless polymer
Oven: 50°C	0.01 wt. %	15 min	Hard, colourless polymer
Stir	0.01 wt. %	12 min	Hard, colourless polymer

Polymerisation Method	M_n	M_w	γ
Ultrasonic Probe	1400	3000	2.1
Oven, 80°C	1100	2700	2.6
Stir	660	1900	2.9

In all cases, molecular weights were low, suggesting poor conversion or poor solubility of the polyurethane in the GPC solvent (DMF). Ultrasonically produced polymer appeared to have marginally the highest molecular weight however and also the narrowest polydispersity.

3.1.4 IPDI-Based Polyurethanes

IPDI has an aliphatic structure (see Section 1.6.3) and is important as a starting material for the production of paint raw materials.[97] The results of polymerisation with butanediol are given in Table 3.4 and also shown in Figure 3.5.

For uncatalysed experiments, ultrasound did not give improved polymerisation times. Sonication of a catalysed solution however, resulted in polyurethane in approximately one third of the time of a sample heated at a comparable temperature. The yellow-brown colouration observed could have been due to a partial ultrasonic degradation of the polymer or monomer.

Table 3.4

Polymerisation of IPDI with 1,4-Butanediol

Oven, Probe or Stir	Catalyst Present	Polymerisation Time	Comment
Probe: 20.1 Wcm^{-2}	-	3 hr	Hard, transparent yellow-brown polymer
Oven: 80°C	-	2.75 hr	Hard, colourless polymer
Probe: 20.1 Wcm^{-2}	0.01 wt. %	35 min	Hard, transparent polymer; yellow tinge. Av. temp. during son.- 50°C
Oven: 80°C	0.01 wt. %	70 min	Hard, colourless polymer
Oven: 50°C	0.01 wt. %	110 min	Hard, colourless polymer
Stir	0.01 wt. %	-	No polymer produced after 6.5 hr, though mixture viscous

GPC results for the catalysed thermal and ultrasonic samples are shown below, with molecular weights relative to polystyrene standards.

Polymerisation Method	M_n	M_w	γ
Oven, 80°C	1000	2000	2.1
Ultrasonic Probe	3500	10400	3.0

The ultrasonically produced polymer has a much higher molecular weight and a broader polydispersity.

3.1.5 Summary of Trends in Initial Investigation

With only one exception (the uncatalysed reaction of IPDI with 1,4-butanediol), the use of an ultrasonic probe greatly increased the speed with which polymer was formed. In some experiments, reaction was almost immediate.

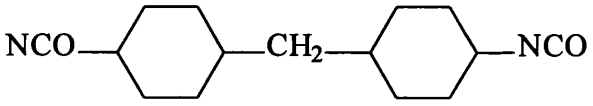
It is known that heat is an effective promoter of OH/diisocyanate reactions[53] and indeed some ultrasonic heating was observed in sonicated reactions. However, the temperatures recorded were lower or at the most equal to temperatures used in thermal experiments, whilst reaction times were shorter. For example, in the reaction of TMXDI with butanediol reaction times were; probe (50°C) - 2.5 min., oven (80°C) - 15 min.

As described in Section 1.4.1, cavitation bubble collapse also leads to violent agitation of solvent molecules. This mixing action of ultrasound is undoubtedly important, as polymerisation is aided by efficient contact of monomer functional groups and thorough dispersal of catalyst. In conventional experiments, mechanically stirred reactions were often found to be faster than thermal equivalents, emphasising the importance of efficient mixing over reaction temperature in many urethane polymerisations.

3.2 Use of Ultrasound in H_{12}MDI-Glycol reactions

After completion of the initial study, it was decided to investigate the reactions of H_{12}MDI in more detail. This diisocyanate was selected firstly, as it is a commercially useful monomer and secondly because experiments had shown that catalysed polymerisations occurred in a relatively short period of time.

Experiments were performed with a range of ethylene glycols. The monomer structures are illustrated below.



H_{12}MDI

$H(OCH_2CH_2)_nOH$

$H(OCH_2CH_2)_nOH$

Poly(ethylene glycol)

3.2.1 Effect of Ultrasound on Reaction Times

Details of experimental procedure are given in Section 2.2.3. In virtually all reactions, polymerisation (gelation) occurred at a very definite point, characterised by solid formation and often a large exotherm.

Figures 3.6 and 3.7 give a comparison of stirred and ultrasonic reaction times for experiments using catalyst solution (dibutyltin dilaurate in acetone) and "neat" catalyst (dibutyltin dilaurate) respectively. Abbreviations used are as follows; ethylene glycol (EG), diethylene glycol (Di), triethylene glycol (Tri), tetraethlene glycol (Tetra), poly(ethylene) glycol (average molecular weight 200, 400, 600), (PEG 200, PEG 400, PEG 600).

Figure 3.6 shows that in all cases (using catalyst solution), the ultrasonic reaction times were considerably faster than the equivalent stirred reactions. There was a general trend for longer reaction times for glycols with higher molecular weights. Stirred reactions with PEG 400 and PEG 600 were unusual in that no definite gelation point was noted and no exotherm measured. The two products remained as viscous liquids, whilst the same ultrasonically produced materials were "tacky" solids.

The remainder of the polymers produced using catalyst solution tended to "foam" on gelation. This was especially true in ultrasonic reactions, where foaming could be very violent, Catalyst solution was used to enable accurate weighing of small amounts of dibutyltin dilaurate, however, it was likely that acetone led to the formation of unstable reaction intermediates, which decomposed to give bubbles of CO_2 gas (see Section 1.6.2). This complicated the study of the reaction.

Subsequently, experiments were performed using "neat" dibutyltin dilaurate and results for these are shown in Figure 3.7. With the exception of the reaction involving tetraethylene glycol, sonicated experiments gave faster polymer production. For stirred reactions there was an increase in polymerisation time as the molecular weight of the glycols increased. In the case of ultrasonic experiments however, reaction time peaked

Figure 3.6

Comparison of Stirred and Ultrasonic Reaction Times for the Reaction Between H_{12}MDI and Glycols using Catalyst Solution

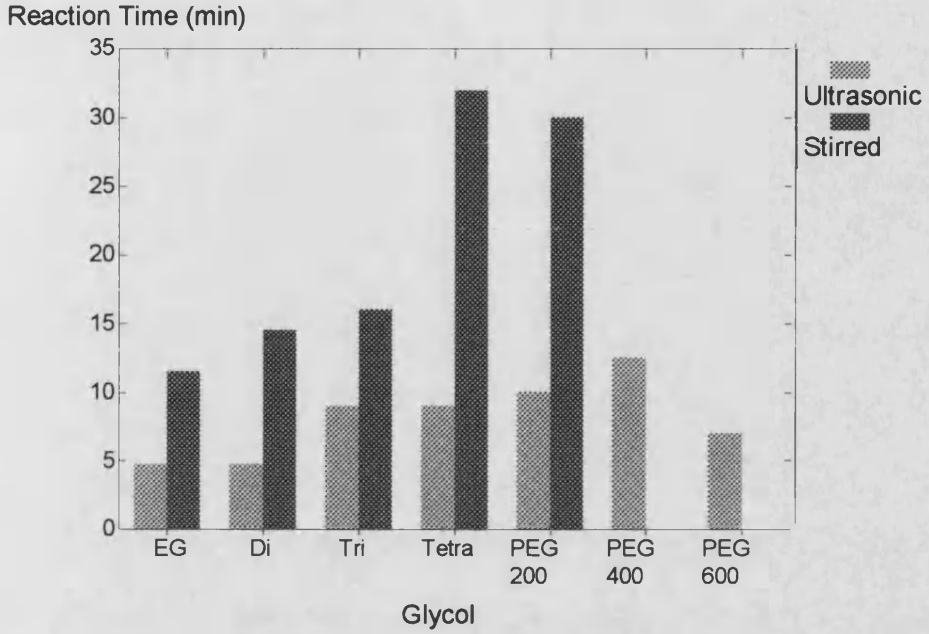
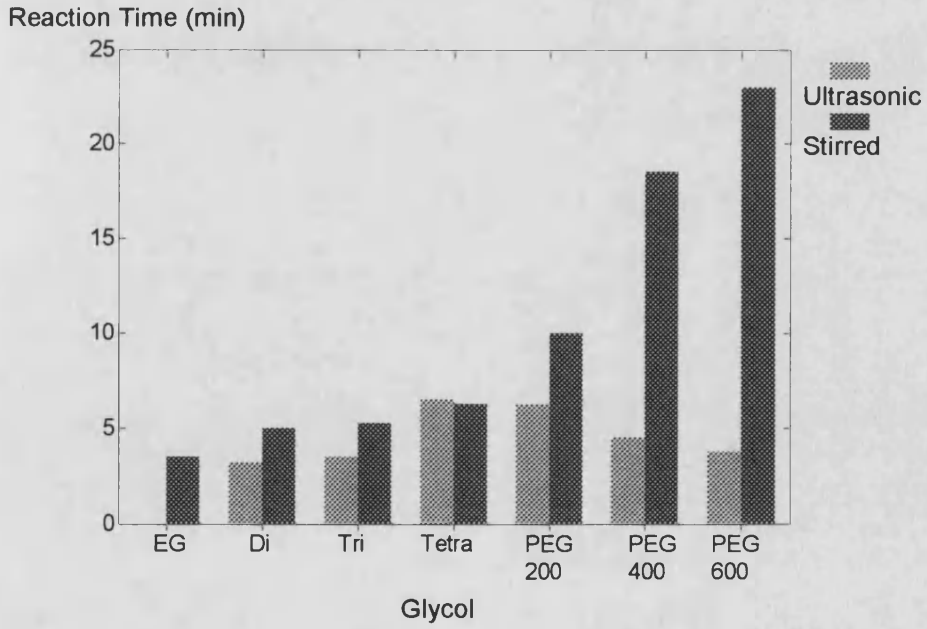


Figure 3.7

Comparison of Stirred and Ultrasonic Reaction Times for the Reaction Between H_{12}MDI and Glycols using "Neat" Catalyst



with the use of tetraethylene glycol and then began to fall. Ultrasound therefore had the greatest effect on reactions involving the longer chain glycols. It was additionally observed that at gelation of ultrasonic experiments using PEG 200, PEG 400 and PEG 600, reaction mixture temperatures rose above 100°C. For the equivalent stirred reactions, the increase was only to 45°C. This confirmed that the use of ultrasound resulted in faster and/or a greater number of functional group reactions and hence a larger reaction isotherm. It should be noted that no polymerisation was observed in the ultrasonic reaction with ethylene glycol.

A further set of experiments investigated the effect of ultrasonic intensity on polymerisation, by carrying out specific reactions at a range of generator powers. In all cases "neat" catalyst was used. Results are shown in Figures 3.8-3.10, together with details of the monomers.

For each of the three systems studied it was found that increasing the ultrasonic power decreased the reaction time. This was an important result as it illustrated a direct link between the amount of ultrasonic energy entering the system and the reactivity of the monomers. This energy gives rise to the production of cavitation bubbles, violent molecular movement and to rises in temperature. The role that these factors play in promoting polyurethane formation will be discussed in Section 3.2.3.

3.2.2 Effect of Ultrasound on Polyurethane Molecular Weight

Gel permeation chromatography was used to analyse the products of reaction with "neat" catalyst in the previous section. Figures 3.11 and 3.12 illustrate the number average molecular weights of H_{12}MDI polymers produced by ultrasound and by stirring.

Figure 3.8

Effect of Ultrasonic Intensity on the Catalysed Reaction Between H_{12}MDI and Triethylene Glycol

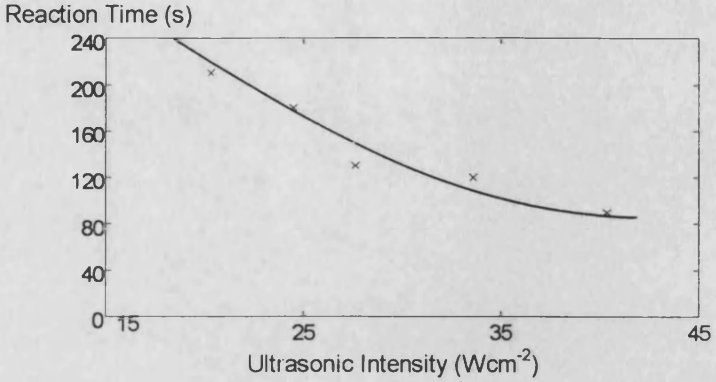


Figure 3.9

Effect of Ultrasonic Intensity on the Catalysed Reaction Between H_{12}MDI and PEG 400

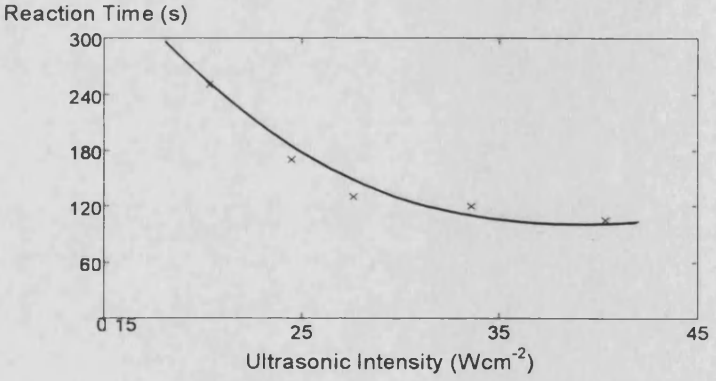


Figure 3.10

Effect of Ultrasonic Intensity on the Catalysed Reaction Between H_{12}MDI and PEG 600

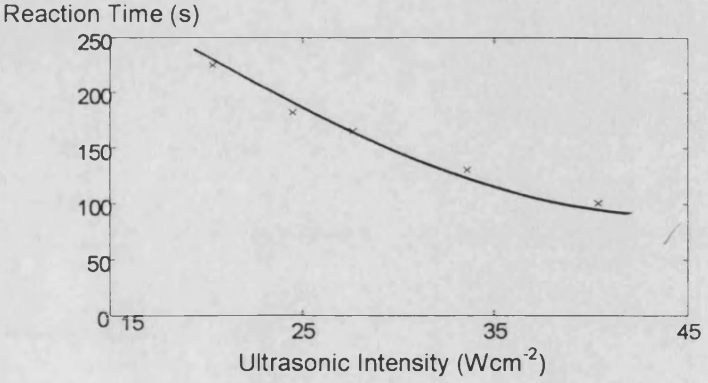


Figure 3.11

Number Average Molecular Weights for H_{12}MDI Polymers produced Ultrasonically and by Stirring

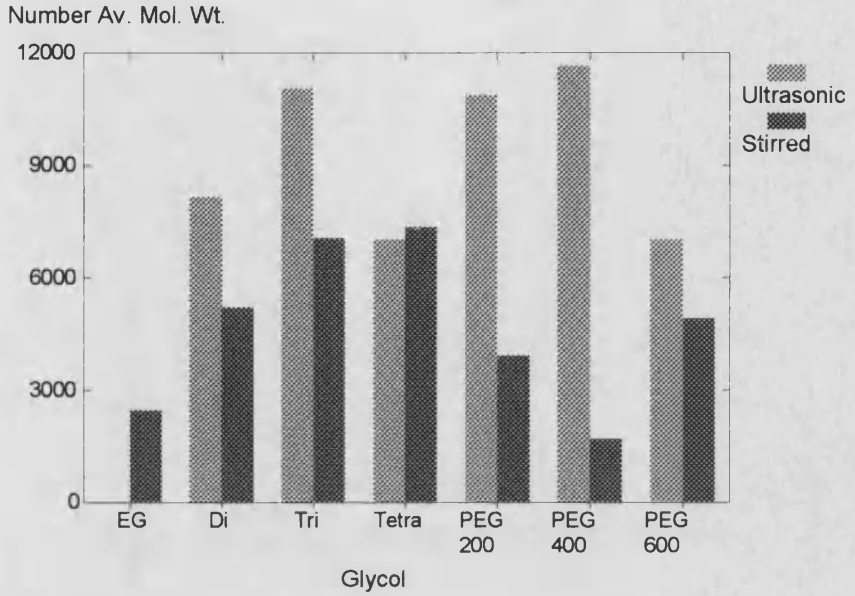
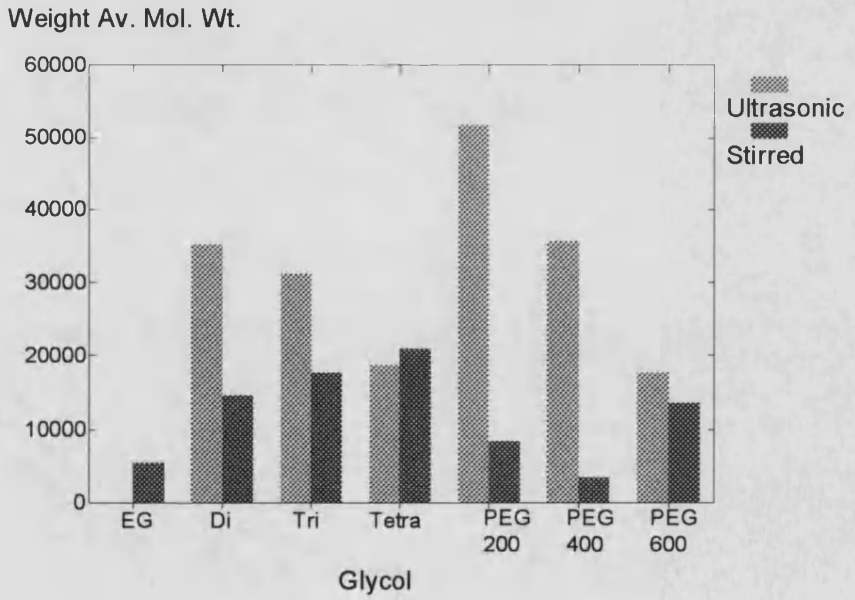


Figure 3.12

Weight Average Molecular Weights for H_{12}MDI Polymers produced Ultrasonically and by Stirring



There appeared to be little correlation between the length of glycol used and the molecular weight of the product in both the ultrasonic and stirred systems. It is apparent however that the polymers produced by sonication had consistently higher M_n and M_w values than their stirred equivalents.

Polymer samples from the series of reactions performed at different ultrasonic intensities were also analysed by GPC. The results for the H_{12}MDI-PEG 600 system are shown in Figure 3.13 as an example. As increased ultrasonic intensity resulted in faster reaction times, it was thought that there might also be a correlation between ultrasonic intensity and the molecular weight of the product. However, as can be seen from the graph, there appears to be no pattern to the results and this was equally true of the other systems (PEG 400 and triethylene glycol). The amount of ultrasonic energy entering the system is therefore not a factor in determining molecular weight. Possible reasons for this will be discussed in the next section.

3.2.3 Consideration of Reaction Time and Molecular Weight Results

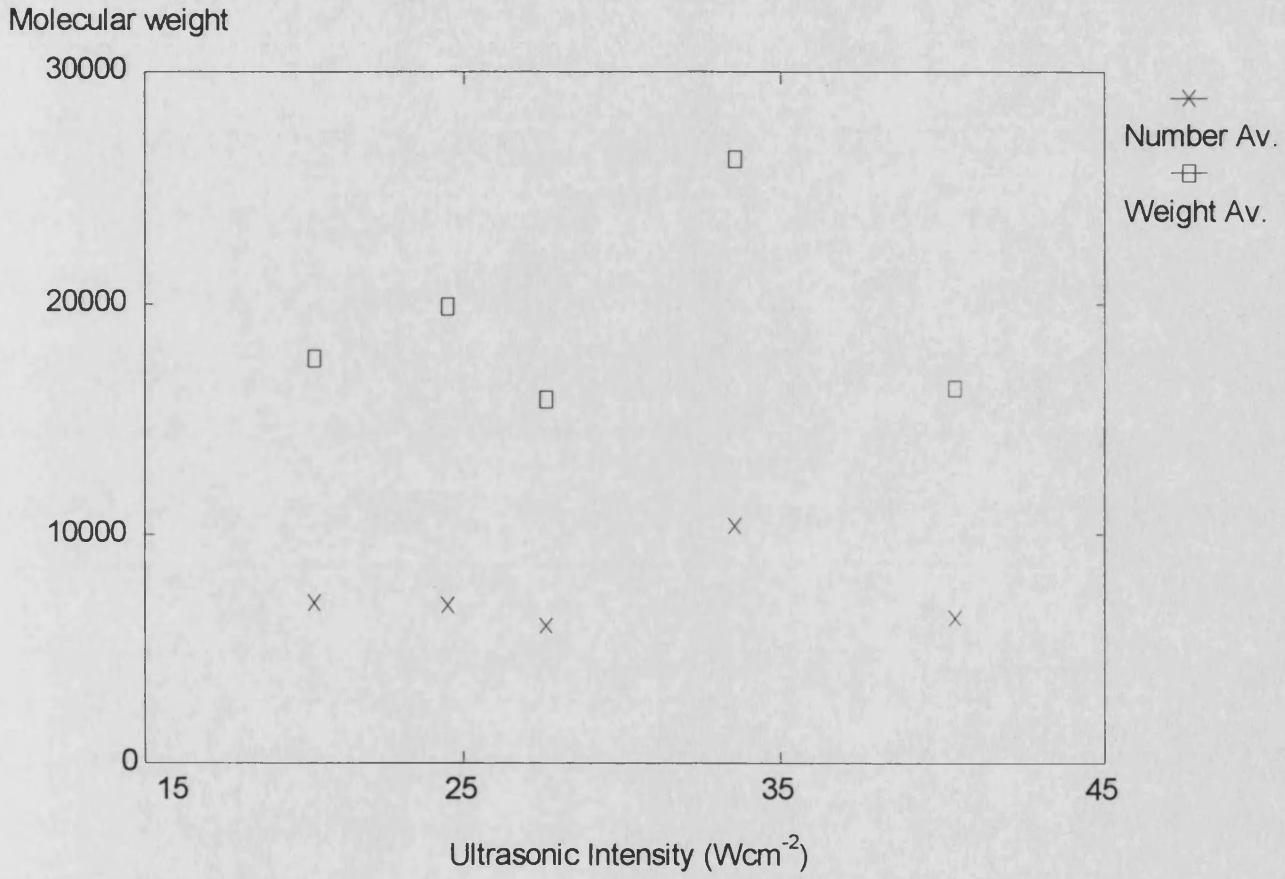
There are a number of factors to be taken into account when attempting to explain the results observed in the H_{12}MDI experiments and these will be considered in turn.

Temperature

Temperature rises were seen throughout ultrasonic and stirred experiments. The fact that rises were observed in mixtures stirred at room temperature indicated that heat was released as the polymerisation reactions progressed. When comparing an instant in the progress of identical stirred and sonicated experiments (e.g. 5 min after starting), it

Figure 3.13

Effect of Ultrasonic Intensity on the Number and Weight Average Molecular Weights of an H_{12}MDI-PEG 600 Polymer



was always the case that the temperature was higher in the ultrasonic mixture. Some degree of temperature rise due to ultrasonic heating was to be expected, but it was important to establish to what extent the higher temperatures seen in ultrasonic reactions were due to this heating alone, rather than to an increased reaction exotherm.

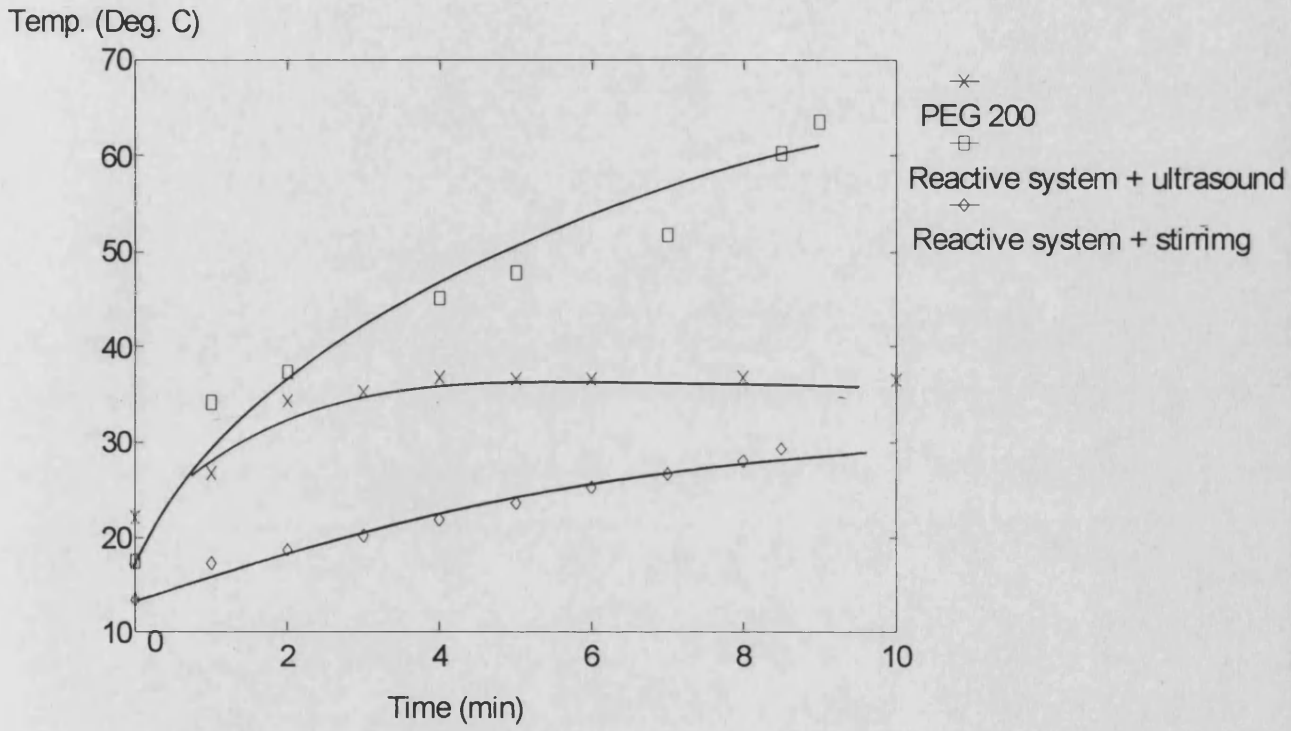
This was achieved by carrying out a blank experiment on a non-reactive system. A volume of PEG 200, identical to the total volume of reactants used in a typical experiment was sonicated and the temperature monitored. No diisocyanate or catalyst were present. PEG 200 was selected as it had a viscosity in the middle range of the materials used.

Figure 3.14 illustrates the results obtained. The middle line on the graph is the heating curve obtained by sonicating the non-reactive system. It can be seen that the temperature rose to about 35°C and then remained constant (due to the cooling action of water circulating in the jacketed vessel) i.e. action of the probe alone heated the average system to 35°C. The uppermost line on the graph shows sonication results from a typical reactive system (H_{12}MDI + triethylene glycol + catalyst solution). The lower line illustrates temperature rises in an identical stirred mixture. After about 5 minutes, it is clear from the graph that the temperature in the sonicated reactive system was greater than the sum of the ultrasonic heating contribution and the stirred reaction exotherm. The additional heat present must be due to the faster rate of polymerisation in the sonicated mixture and therefore the greater release of energy per unit time.

It was observed in many of the H_{12}MDI-glycol reactions that a "take-off" point occurred, whereupon the temperature began to rise rapidly and gelation soon occurred. The heating effect of the ultrasonic probe may have been significant in helping the

Figure 3.14

Comparison of Temperature Rises in a Non-Reactive System (PEG 200) and a Reactive System (H_{12}MDI + Triethylene Glycol + Catalyst)



reactants to reach the "take-off" temperature more quickly, thereby speeding reaction. This would also explain the shorter reaction times seen at higher ultrasonic intensities (Figures 3.8-3.10). At higher generator settings, the ultrasonic heating effect is greater and the "take-off " temperature can be reached in a shorter time. It should be noted however that these temperature differences are not large (as the vessel is water cooled) and that ultrasonic stirring must also be considered when explaining the trends in reaction time.

The link between ultrasonic heating effects and molecular weight is less clear. It was often found that the temperature of reaction mixtures continued to rise after gelation, although stirring/ultrasound had been stopped. These were particularly large in sonicated solutions, often reaching 150°C. Stirred reactions tended to achieve much lower temperatures and in some cases (as discussed in Section 3.2.1) only reached 45°C. The extreme sonochemical final temperatures must be a result of a larger number of functional group reactions and this is supported by the production of higher molecular weight polymers in ultrasonic experiments. The step-growth nature of polyurethane formation means that high molecular weight material is only obtained towards the end of the reaction, when high degrees of polymerisation are attained (i.e. many functional group interactions must take place, particularly between species of an intermediate chain length).

As shown in Figure 3.13 however, no correlation was found between ultrasonic intensity and polymer molecular weight. This suggests that the ultrasonic thermal energy entering the system encouraged functional group interaction and was able to

quickly raise the reaction temperatue to the "take-off" point, but did not play a role in subsequent molecular weight determination.

Stirring

As described in the Introduction, ultrasound can give extremely efficient mixing of solutions. This ability was likely to be a major factor in producing the fast reaction times seen in ultrasonic polyurethane experiments, where frequent contact between monomer functional groups and good dispersal of catalyst was necessary for polymer production. Increasing the ultrasonic intensity led to even more vigorous stirring and a decrease in reaction time. It is likely that both stirring and ultrasonic heating are responsible for this direct correlation between intensity and reaction time.

The absence of a link between ultrasonic intensity and polymer molecualar weight, despite ultrasonic reactions having consistently higher molecular weight values that stirred reactions, poses the same problems of explanation faced in the discussion of temperature effects however. As described in the above section, it seems likely that mixing promotes a large number of functional group reactions and the subsequent exotherm brings the mixture to the "take-off" temperature. The reaction is then largely self-sustaining and molecular weight is dependent on the progress of the final rapid polymerisation stage.

Chemical Effects

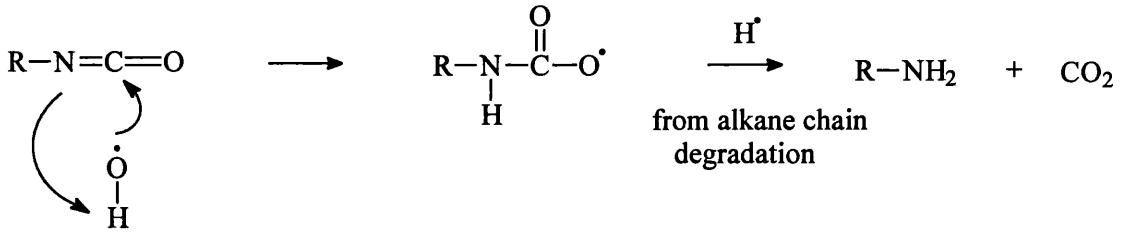
Apart from the physical effects of heating and stirring, chemical cavitation phenomena may be responsible for promoting faster reaction. The extreme pressures and temperatures believed to occur within cavitation bubbles[14] are known to lead to

bond cleavage when organic liquids are sonicated. Examples of bonds broken by ultrasound include carbon-hydrogen,[98] carbon-carbon[98] and carbon-halogen[99] .

The table below shows enthalpies of some common organic bonds.[100]

Bond	Bond Enthalpy ($kJ\ mol^{-1}$)
C-C	348
C=C	612
C-O	360
C=O	743
C-H	348
C-N	305
C=N	613
C-Cl	338

It can be seen that the bond enthalpy of C-O is similar to that of the bonds already mentioned as being commonly broken by ultrasound (~350 $kJ\ mol^{-1}$). If during ultrasonic polyurethane formation, some of the monomers are degraded by the cavitaiton process, then it is likely that cleavage of the R-OH bond of the glycol will occur, to give an OH radical. This can react as follows:



The amine end group is then able to react with an isocyanate group to give a urea linkage, whilst the release of CO_2 leads to a "foaming" product. Other products of glycol degradation are likely to be sinple alkanes, whilst H_{12}MDI may degrade to give alkanes, carboxylic compounds and amines.

The extent to which such monomer degradation occurs (if at all) in ultrasonic polyurethane experiments can only be determined by detailed analysis of the reaction mixture. If break-down species do exist in a significant number then they may initiate all manner of side and main-chain reactions, some of which could lead to faster reaction times and higher molecular weights. Further work is needed on the effects of cavitation on a wide range of organic liquids in order to predict the effects on polyurethane monomers.

In summary, the factors influencing ultrasonic polyurethane formation and their possible consequences are shown schematically in Figure 3.15.

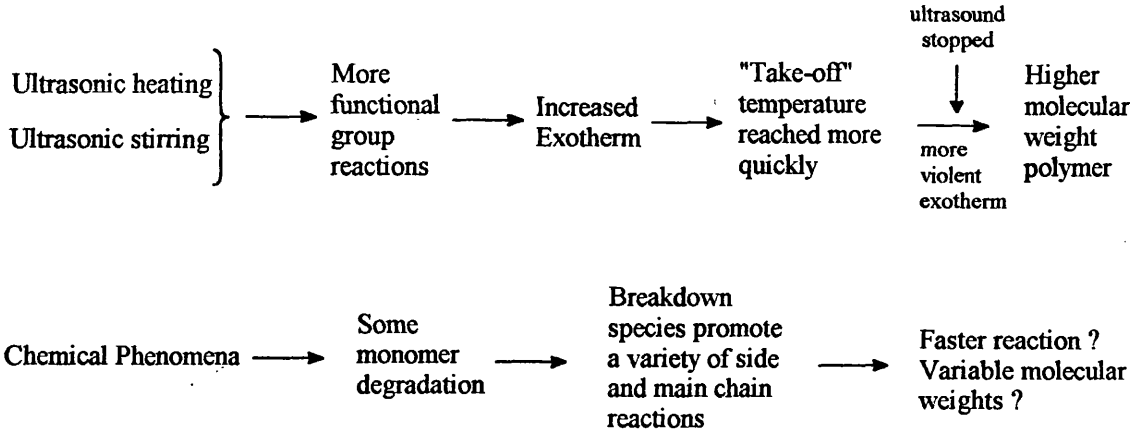
3.3 Kinetics of Ultrasonic Polyurethane Reactions

In order to obtain a greater understanding of the role that ultrasound plays in promoting polyurethane-forming reactions, it was decided to investigate the kinetics of some polymerisations. This would allow quantitative comparisons to be made between ultrasonic and conventional experiments.

A number of difficulties were encountered and several experimental methods were attempted in order to achieve successful measurement. A full discussion of polyurethane kinetics is given in Section 1.6.5.

Figure 3.15

Factors Influencing Ultrasonic Polyurethane Formation



3.3.1 Use of Infrared Spectroscopy

Infrared spectroscopy is a useful tool for studying isocyanate-based reactions, as the isocyanate functionality has a very characteristic peak at ~2270 cm^{-1} in the I.R. spectrum. It is relatively straightforward to monitor the disappearance of this peak and in the case of reaction with OH groups, to follow the growth of the amide peak (1600-1700cm^{-1}) present in the urethane linkage.

Several workers have therefore used infrared spectroscopy to study the reaction between isocyantes and OH-containing materials. Flynn[101] for example, investigated the reaction between phenyl isocyanate (a mono-isocyanate) and various alcohols, using benzene as a solvent.

More recently, Couglin,[65] examined the reaction of the diisocyanate TMXDI with poly(propylene glycol) (M.W. 2000). Experiments were performed *in situ*, by smearing the reaction mixture onto salt plates and monitoring curing over a period of time. Sachdev[102] also used an *in situ* method to investigate polyurethane foam formation. Foam prepolymer and water were mixed for 30s and then transferred to the ATR unit of an FTIR.

The system selected for investigation in this study was the uncatalysed reaction between IPDI and 1,4-butanediol (previously discussed in Section 3.1.4). IPDI was chosen as it had been found that polymerisation with the diol took place over a period of time (3 hours), that enabled a number of measurements to be made.

Tables 3.5 and 3.6 list the major peaks seen in the I.R. spectra of the monomers and their probable assignment. Table 3.7 shows the peaks present in a sonicated solution. Figures 3.16-3.18 are the respective I.R. spectra.

Peak (cm^{-1})	Assignment
2955 (m)	CH stretch
2256 (s)	NCO stretch
1459 (m)	C-CH_3 stretch
1385 (m)	RCOR stretch
1363 (m)	RCOR stretch

Table 3.5

Major Peaks in the IR Spectrum of IPDI

Peak (cm^{-1})	Assignment
3311 (s,br)	OH stretch
2937 (s)	CH_2 stretch
2871 (s)	CH_2 stretch
1660 (w,br)	-
1472 (m)	-
1052 (s)	C-O stretch/ O-H deformation
946 (m)	-

Table 3.6

Major Peaks in the IR Spectrum of 1,4-Butanediol

Peak (cm^{-1})	Assignment
3345 (s,br)	BD
2937 (s)	BD
2261 (s)	IPDI
1694 (m)	C=O stretch in amide
1456 (m)	IPDI
1386 (m)	IPDI
1363 (m)	IPDI
1053 (s)	BD

Table 3.7

Major Peaks in the IR Spectrum of Sonicated IPDI and BD

Figure 3.16

IR Spectrum of IPDI

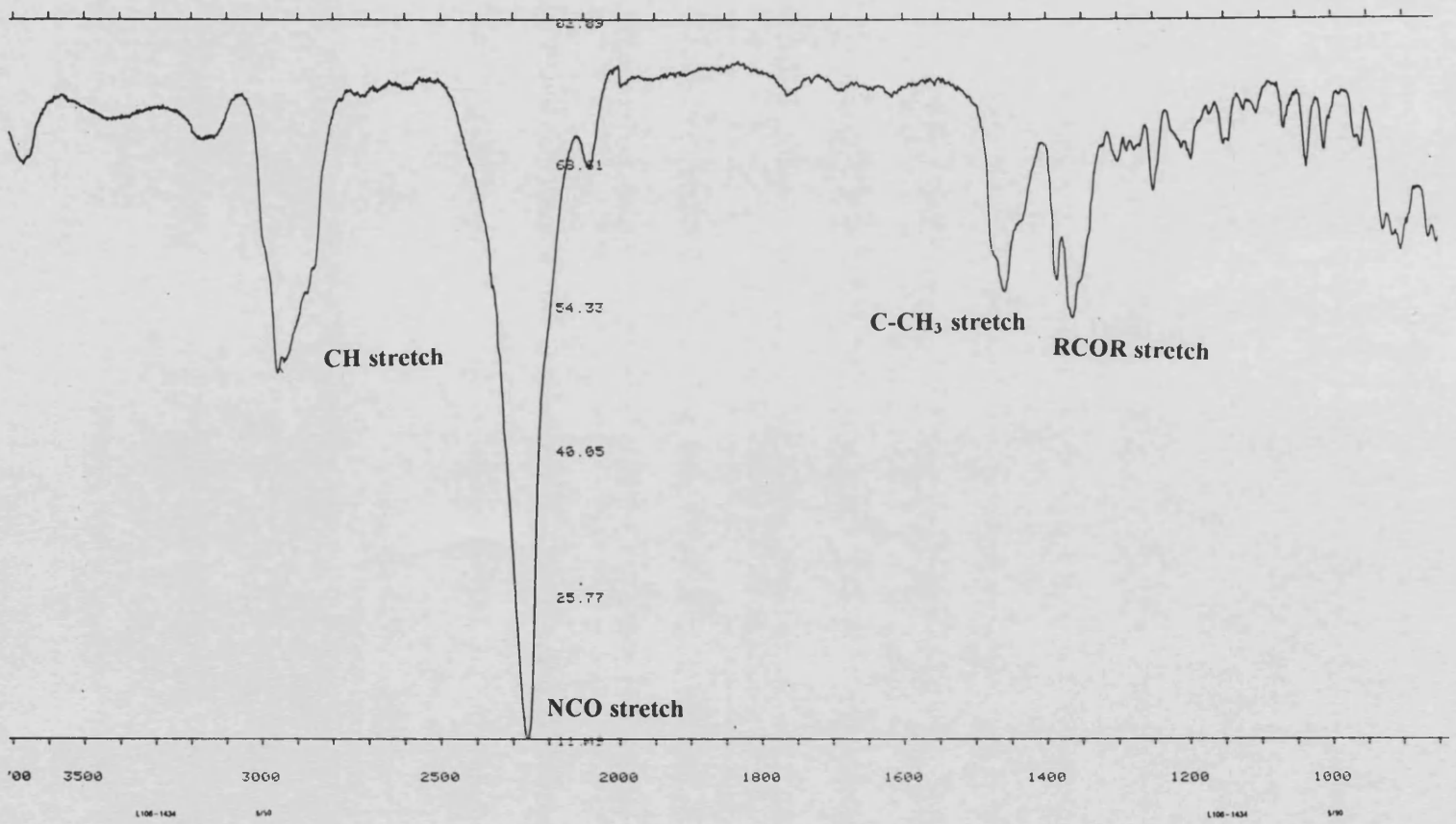


Figure 3.17

IR Spectrum of 1,4-Butanediol

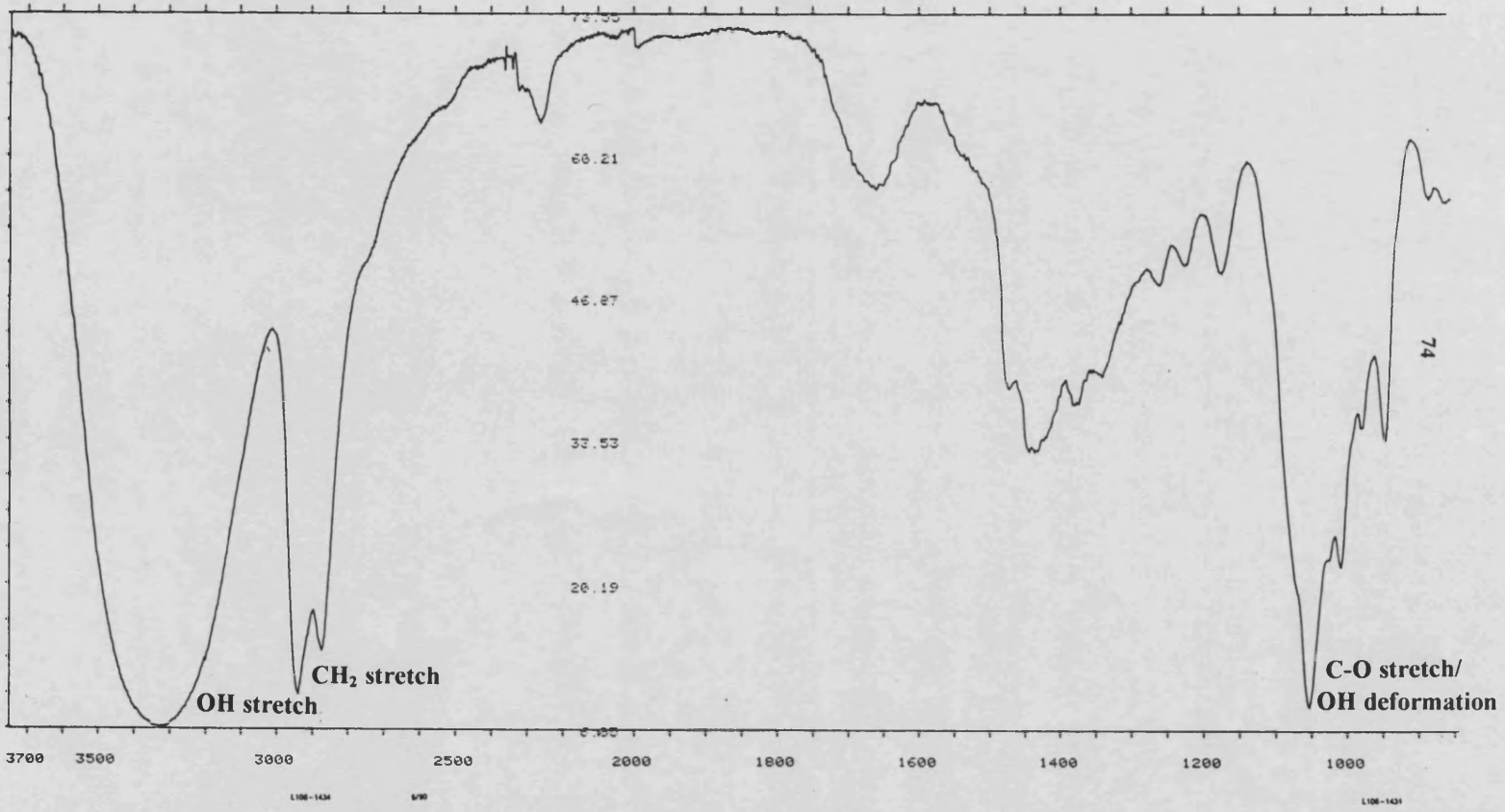
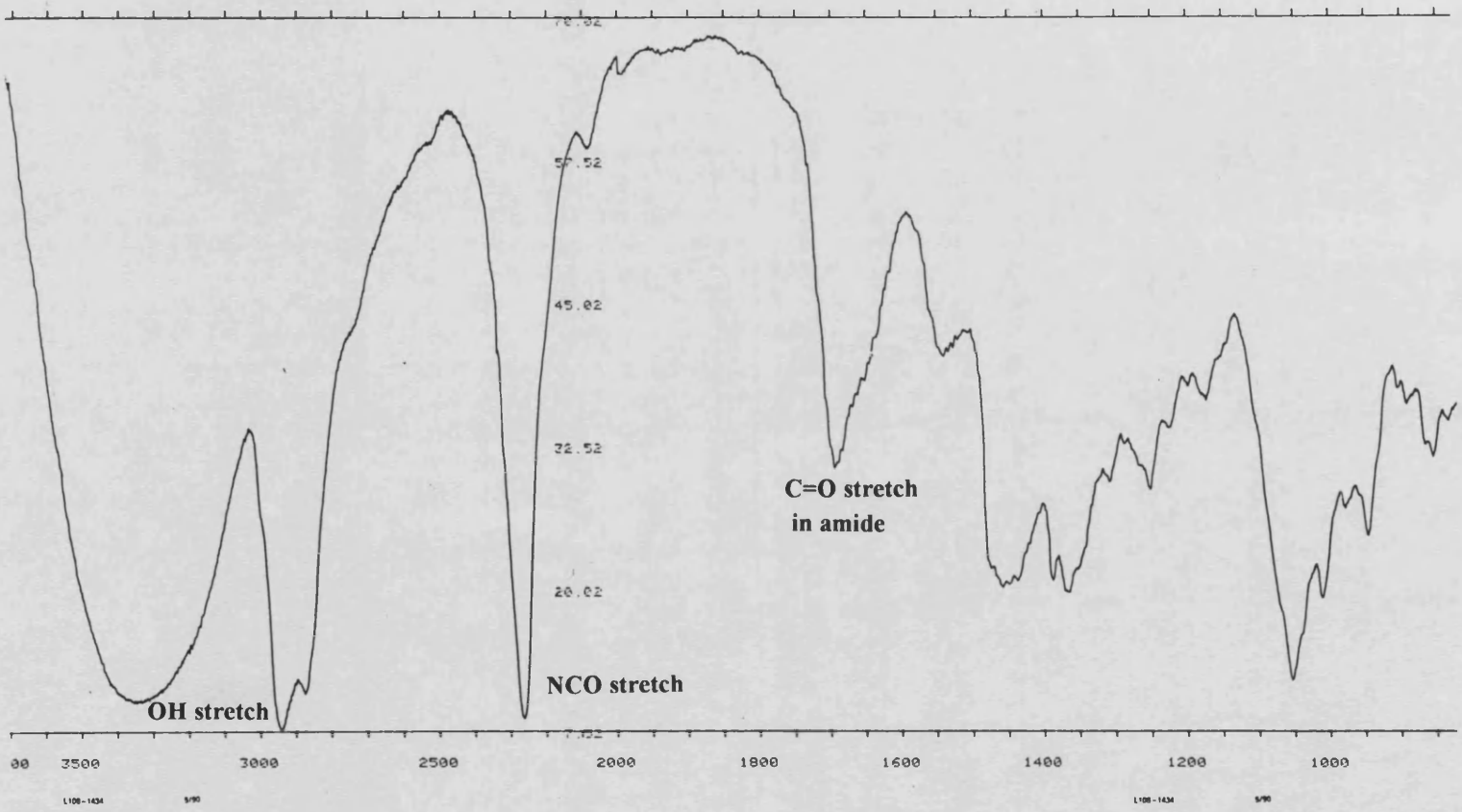


Figure 3.18

IR Spectrum of a 1:1 Mixture of IPDI and BD sonicated for 40 min at 20.3 Wcm^{-2}



The most important wavenumbers are 2256 cm^{-1} (isocyanate) and 1694 cm^{-1} (amide). With increasing reaction time, the concentration of NCO would be expected to decrease, whilst the amide peak should gradually appear and become larger. To monitor the reaction between IPDI and 1,4-buatanediol, the height of the NCO peak with sonication time was recorded. It was necessary on each occasion to find the ratio of the NCO peak to other peaks in the spectrum that were not affected by polymerisation (e.g. alkane stretch at 1459 cm^{-1}). In this way, inevitable discrepancies arising from differences in the sample size under analysis were removed.

The reaction between IPDI and 1,4-butanediol was carried out a number of times. On each occasion however, the expected decrease in the size of the NCO peak was not observed, instead values fluctuated in an apparently random manner. To account for the possibility that the "unchanged" peak (1459 cm^{-1}) being used for ratio measurements was in fact altered during polymerisation, comparisons were made instead with the amide peak. The ratio of amide peak size to NCO peak size should increase as the reaction progresses. Once again however, apparently random results were obtained.

As a check on the precision of the analysis, 5 samples were taken from a sonicated solution simultaneously and analysed by I.R. Three samples were in reasonable agreement ($\pm$ 8%), but the other two had very different NCO peak sizes. This suggests that sampling was to blame for the poor results obtained i.e. samples are not representative of the mixture as a whole due to inhomogeneity of the system.

Solution Polymerisation

In an attempt to obtain a more homogenous mixture, THF was added as a solvent to the two monomers and fresh reactions were performed. THF was selected as it neither obscured monomer functional group peaks on the I.R. spectrum, nor entered into reactions with the isocyanate. Results were a little more consistent but unexpected variations in peak size still occurred. An example of one of the more successful reactions is shown in Figure 3.19. The y axis shows the ratio of amide peak to isocyanate peak and there appears to be a reasonably linear growth of urethane linkages.

Such results were not reproducible however. This was probably due in part to inefficient solution of the monomers in THF and also to the difficulty of using a solvent in an ultrasonic reaction. Ultrasonic degradation of solvent molecules may give species which interfere with polymerisation and additionally, ultrasound can promote solvent evaporation, especially when the boiling point is low.

To further investigate whether difficulties lay with sampling or with the analysis technique itself, mixtures of IPDI, BD and THF were either sonicated or heated at 30°C (equivalent to temperature rises in sonication), for a period of 30 minutes. In each case a small portion of reaction mixture was immediately placed on NaCl plates and the curing of the sample was followed for approximately 6 hours *in situ*. As only one sample was being monitored, no sampling errors could occur and indeed no anomalous results were recorded. Figure 3.20 illustrates the ratio of amide to NCO for the two systems initiated in different ways. It can be seen that the sonicated mixture cured more rapidly than the heated mixture. It is interesting to note that even though

Figure 3.19

Change in Ratio Amide Peak:Isocyanate Peak with Time for the Reaction between IPDI and BD in THF at 20.1 Wcm^{-2}: Samples Monitored by Infrared Spectroscopy

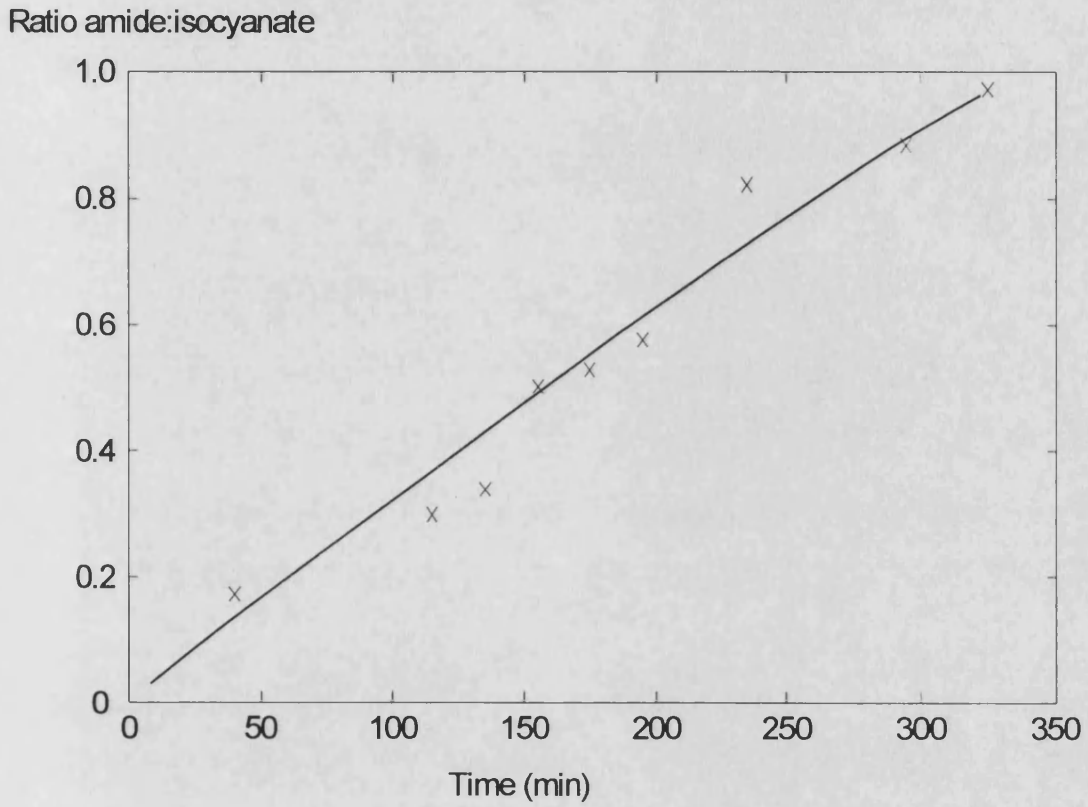
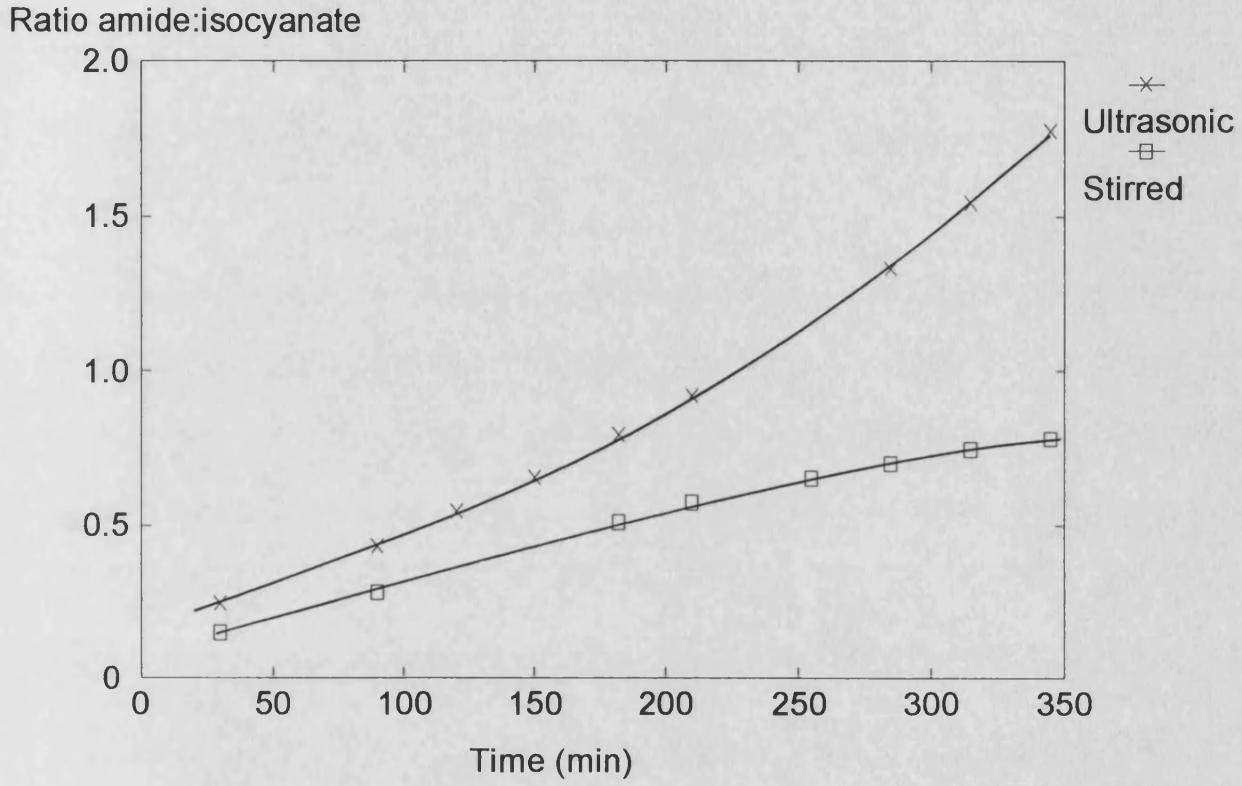


Figure 3.20

***In Situ* Curing of IPDI and BD in THF:**
Effects of Preliminary Heating and Sonication



sonication/heating was no longer occurring, the initiation period of 30 minutes was sufficient to cause a difference in subsequent reaction rates.

Discussion

It would appear that following the kinetics of bulk (i.e. no solvent), polymerisations by means of sampling is far from straightforward. Indeed, Frisch[58] states that very few kinetic investigations have been reported for these reactions due to variations in viscosity and heterogeneity. The previous studies described at the beginning of this section all involve solution work[101] or *in situ* experiments.[65,102]

As described, solution work gave very variable results and it seems that a solvent must be used which gives excellent homogeneity of the monomers. Ideally reactions should be performed in a sealed vessel, to prevent escape of solvent vapour.

The *in situ* method was more successful however for studying the curing of IPDI and BD (Figure 3.20). Ultrasound was able to initiate a faster rate of reaction than in stirred solutions, despite an initial sonication period of only 30 minutes. This effect is similar to that observed in the previous Section (2.3.1), where on reaching a "take-off" temperature, reactions between H_{12}MDI and glycols proceeded rapidly with ultrasound playing little further part.

Although the *in situ* method is useful, in order to obtain a measure of the continuous effects of ultrasonic polymerisaton, a sampling technique is needed.

3.3.2 Use of Dibutylamine Back Titration

The dibutylamine back titration for determining the percentage of isocyanate in a mixture is described in detail in Section 2.3.5. It has been widely used to investigate the

kinetics of mono and diisocyanate reactions, especially by early workers who did not have access to spectroscopic techniques. Baker[54,103] for example carried out the first thorough investigation of the uncatalysed and tertiary amine catalysed reaction of aromatic isocyanates with the OH functionality in the late 1940s. Burkus and Eckert[104] worked on the reaction of a variety of diisocyanates with 1-butanol in toluene, whilst Ephraim[105] performed experiments with phenyl isocyanate and alcohols in a number of solvents.

In 1975, Anzuino[106] used the titration to study diisocyanate-butanol reactions and also considered a polyurethane-forming reaction, that between MDI (structure see Figure 1.14) and polyoxytetramethylene glycol in dimethylacetamide. More recent work also concentrates on polyurethane formation rather than one-step processes. Mencer[107] and co-workers investigated TDI in reaction with polyoxypropylene diol and triol in a batch reactor under vacuum and was able to sucessfully follow the decrease in isocyanate concentration. Krol[61] *et al* attempted to devise a kinetic model for polyurethanes based on reaction between phenyl isocyanate and simple diols and also between TDI and polypropylene glycol (M.W. 1000). Reactions were performed in chlorobenzene.

Initial experiments in the ultrasonic study applied the dibutylamine titration to the reaction between IPDI and 1,4-butanediol (the system also investigated by I.R.). Samples were analysed every 30 minutes and after a period of approximately 3 hours, polymerisation occurred.

Experiments were repeated a number of times, with the expectation of seeing a decrease in the percentage of isocyanate in the mixture as the reaction progressed.

Results were found to be extremely variable however and though the general trend was usually for a fall in % NCO, wide fluctuations occurred and reproducibility was poor.

Figure 3.21 illustrates one of the better sets of data obtained. It can be seen that very little isocyanate was consumed until the final stages of the reaction, when a sudden "take-off" occurred. This is consistent with the sudden exotherms and violent foaming reactions noticed already in a number of systems (Section 3.2.3, temperature discussion).

As with I.R. work, it is likely that inhomogeneity of reaction mixture samples was to blame for the inconsistent results. Dilution of the reaction mixture with THF was attempted, but this gave no improvement.

An additional system was also studied, the uncatalysed reaction between H_{12}MDI and 1,4-butanediol. From initial work (Section 3.1.1) it was known that polymerisation occurred in approximately 5 hours.

The reaction was performed both ultrasonically and by stirring at 50°C (to mimic the ultrasonic temperature rise). Two samples were removed at each time interval to allow titrations to be performed in duplicate.

Figure 3.22 shows results for the ultrasonic and stirred reactions. Points on the graph are averages of the two titrations. Agreements between pairs of samples ranged from good (± 1%) to poor (± 20%). Polymerisation was not observed in the stirred mixture in the time available (7 hours). A sudden fall in the % NCO in the sonicated experiment was seen after 3.5 hours however. The decrease continued until polymerisation occurred.

Figure 3.21

Change in % NCO with Time for the Sonicated Reaction between IPDI and BD at 20.1 Wcm^{-2}: Samples Monitored using the Dibutylamine Titration

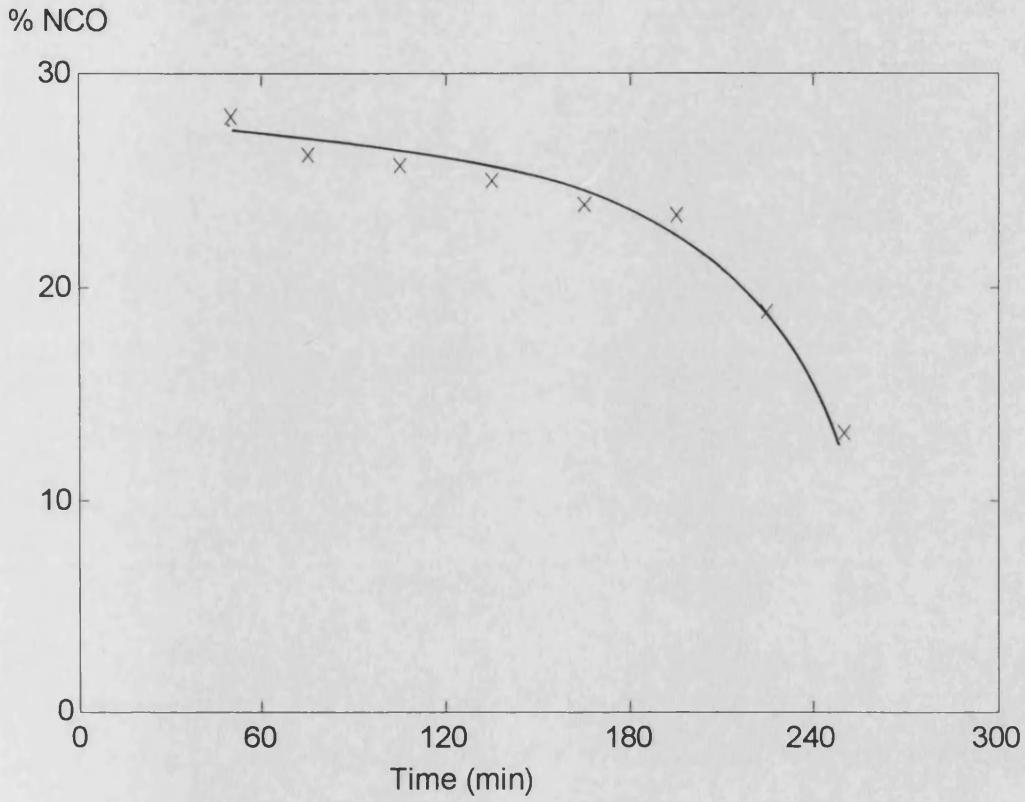
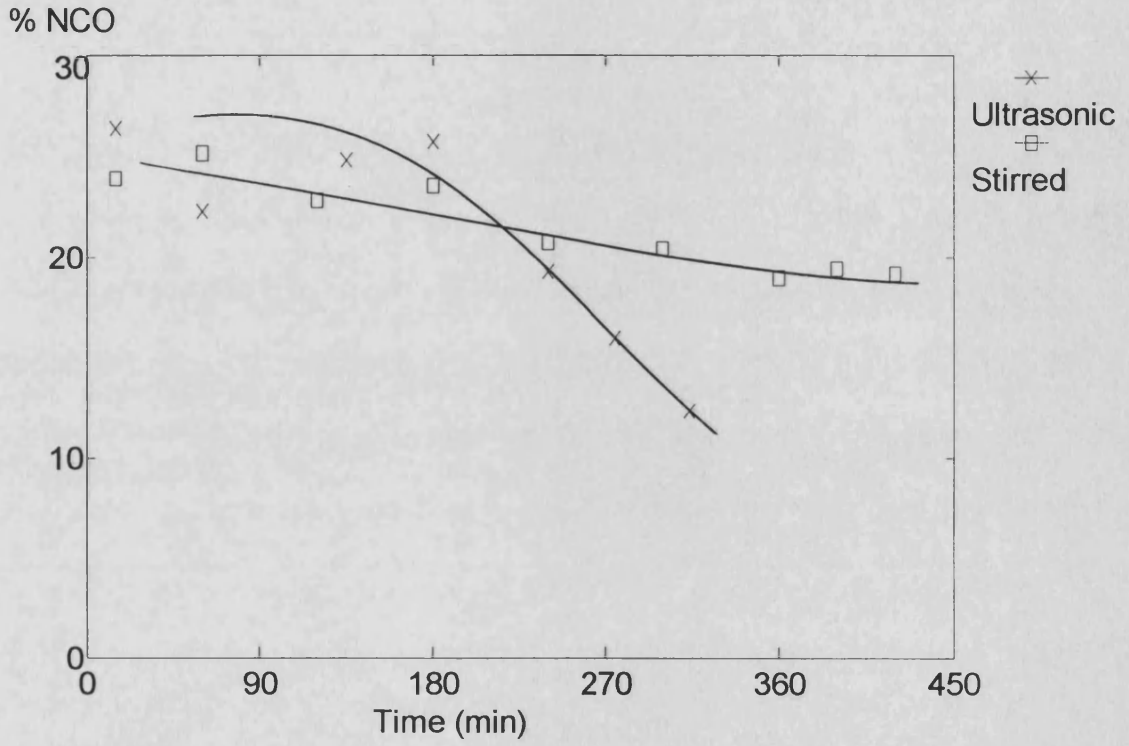


Figure 3.22

Change in % NCO with Time for the Sonicated and Stirred Reactions between H_{12}MDI and BD at 20.3 Wcm^{-2}: Samples Monitored using the Dibutylamine Titration



Discussion

The dibutylamine back titration is a useful method for studying reaction kinetics but care must be taken in selecting systems appropriate for study. Excellent heterogeneity of the reaction mixture is needed and in this respect the H_{12}MDI experiments were more successful than those using IPDI. Much of the work by other researchers, discussed at the beginning of this section, involved mono-isocyanate reactions, or systems using a solvent where mixing of the reaction components was far easier.

The results obtained in this study indicated that the ultrasonic experiments involved a period where little consumption of monomer occurred, prior to a more rapid reaction. This is in contrast to data found by workers such as Mencer[107] who observed a fast initial reaction between TDI and polypropylene glycol, followed by a gradual levelling off. The initial rate was highly dependent on the nature of the catalyst used however. It should also be noted that reaction conditions were fairly extreme (vacuum of 1333 Pa and stirring at 200 rpm). This was obviously sufficient to initiate polymerisation immediately. Krol[61] also found a fast initial rate of reaction, with polymerisation following second order kinetics up to 60-70% conversion. At higher conversions, a slight decrease in the rate constant was usually observed, probably resulting from the influence of side reactions. Reactions were performed at 60°C, 80°C and 100°C, temperatures which are arguably sufficient to cause immediate reaction.

The kinetic measurement of a sudden "take-off" occurring in ultrasonic reactions is consistent with the qualitative effects noted in Section 3.2.2 (i.e. sudden exotherm accompanied by rapid polymer formation). It is likely that this "take-off" occurs when

energy entering the system is sufficient to enable the heat of the reaction exotherm to perpetuate further functional group reactions. Under harsher conditions (e.g. those of the workers described above), initiation may be almost instananeous. By performing ultrasonic reactions at relatively low temperatures however, it is possible to isolate the role that ultrasound plays.

3.3.3 Use of Gas Chromatography

As limited success had been met with other analytical techniques, it was decided to investigate the use of gas chromatography for measuring diisocyanate reaction kinetics.

Cunliffe *et al*[108] used gas chromatography to study the kinetics of the reaction of IPDI with mono-alcohols in heptane. By means of correlation with N.M.R. measurements, they found it possible to measure rate constants for the 4 different isocyanate groups (2 each for the cis and trans isomers).

Initial work in the ultrasonic study involved the investigation of the reaction between Desmodur Z and butanol. Desmodur Z, a polyfunctional aliphatic diisocyanate was selected as it had the highest vapour pressure of the diisocyanates available (2.25 mm Hg (20°C)).[109] Details of gas chromatography are given in Section 2.3.4.

Test samples of Desmodur Z and butanol were analysed initially to investigate the feasibility of the system. It was found however that separation of the diisocyanate and alcohol was impossible as the broadness and relatively large size of the butanol peak completely obscured that of Desmodur Z.

Attention then turned to the use of a capillary system. Capillary columns, typical diameter 0.25 mm, are not packed with a support material; instead the stationary phase is coated directly onto the wall of the column. The length of the column, 30 m, allows very efficient separation of mixtures. It was decided to look at the effect of ultrasound on a system studied by Cunliffe,[108] namely the reaction of IPDI with propan-2-ol. Heptane was used as a solvent and tetradecane was identified as being an appropriate internal standard. The addition of a known amount of tetradecane to the reaction mixture allowed direct comparison to be made between the peak area of the isocyanate and tetradecane signals as the reaction progressed i.e. the factor under investigation was the ratio isocyanate:tetradecane.

Figure 3.23 is gas chromatogram showing the relative positions of the reaction components. The sample size was 0.3 μl. Figure 3.24 is the equivalent trace for a sample of 0.7 μl. The broadening of the IPDI peak is likely to be due to more effective separation of the isomers of the diisocyanate. It was found that a sample volume of at least 6 μl was needed to obtain reproducible values of the isocyanate:tetradecane ratio from the same sample. This is illustrated in Figure 3.25 which shows the % of total area occupied by the diisocyanate and tetradecane peaks in the chromatogram of a test sample, for a range of injection volumes. Figure 3.26 shows the ratio of the two peak sizes for the same range. The ratio falls dramatically as sample volume is increased from 0.025 μl to 0.5 μl. A small volume error in this range would therefore have a large effect on results.

Ultrasonic and stirred reactions were initially attempted at 60°C, but it was found that heptane and propan-2-ol evaporated from the reaction mixture too readily at

Figure 3.23

Gas Chromatogram Illustrating the Relative Positions of Reaction Components in the IPA/IPDI Reaction: 3 μl injection

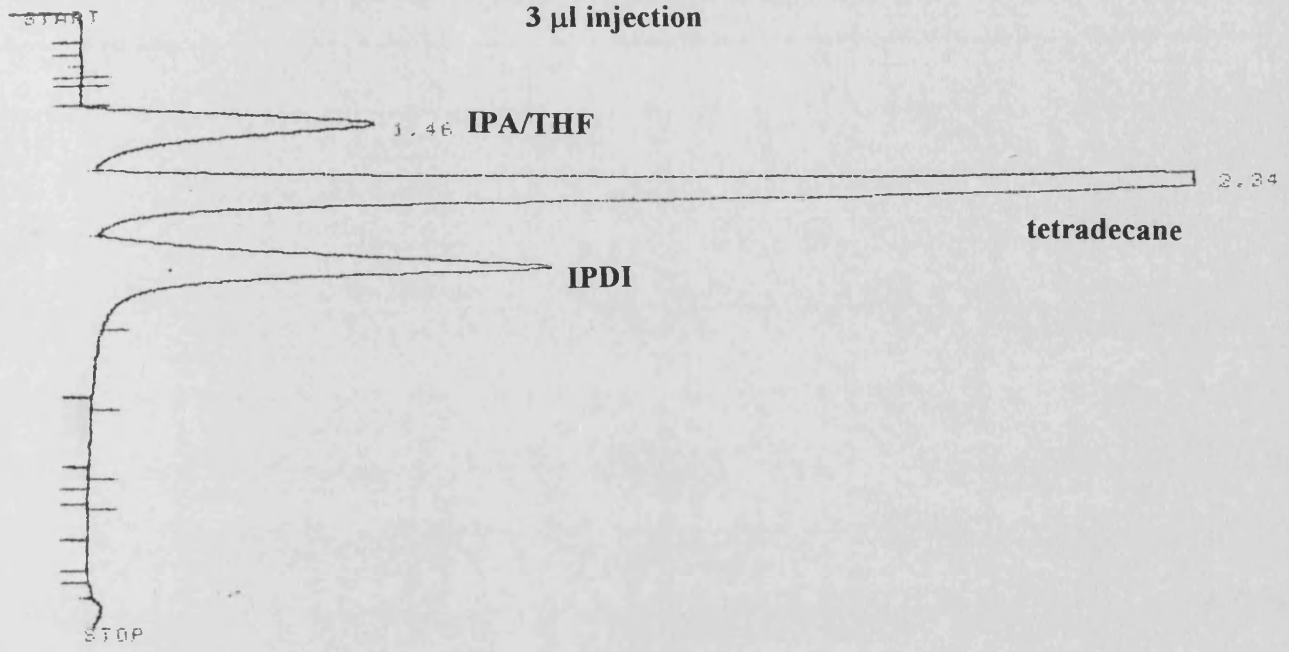


Figure 3.24

Gas Chromatogram Illustrating the Relative Positions of Reaction Components in the IPA/IPDI Reaction: 7 μl injection

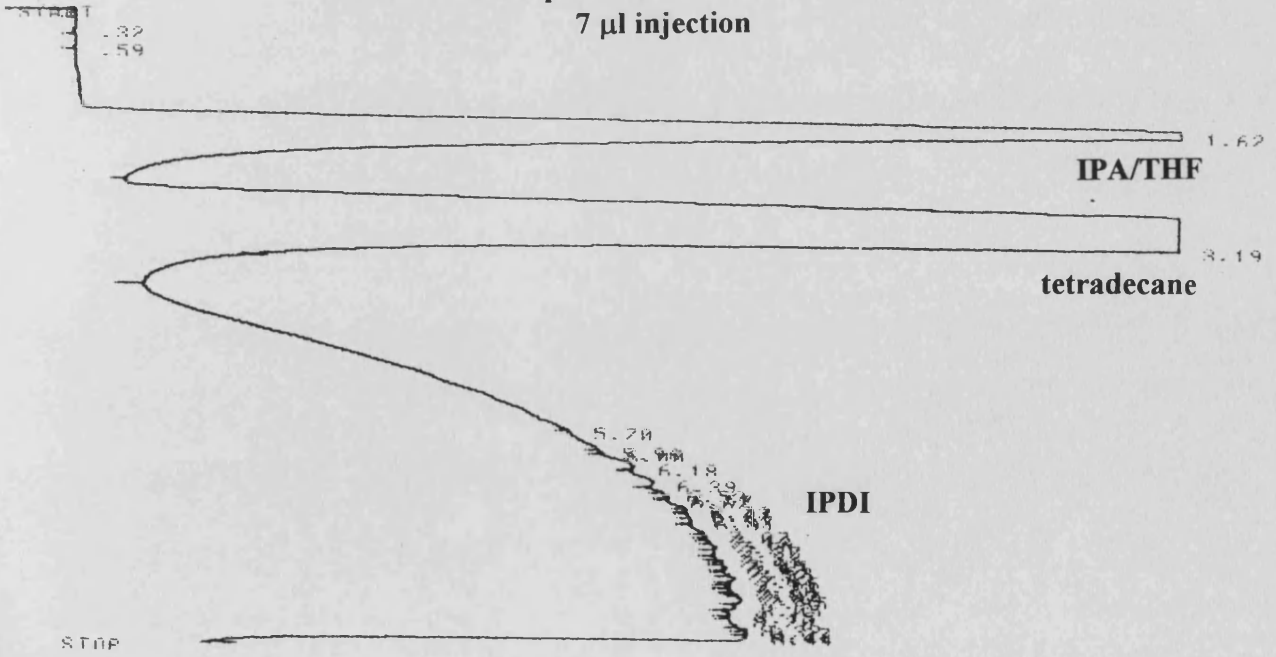


Figure 3.25

Variation of % of Chromatograph Area Occupied by Diisocyanate and Tetradecane Peaks with Volume of Sample Injected

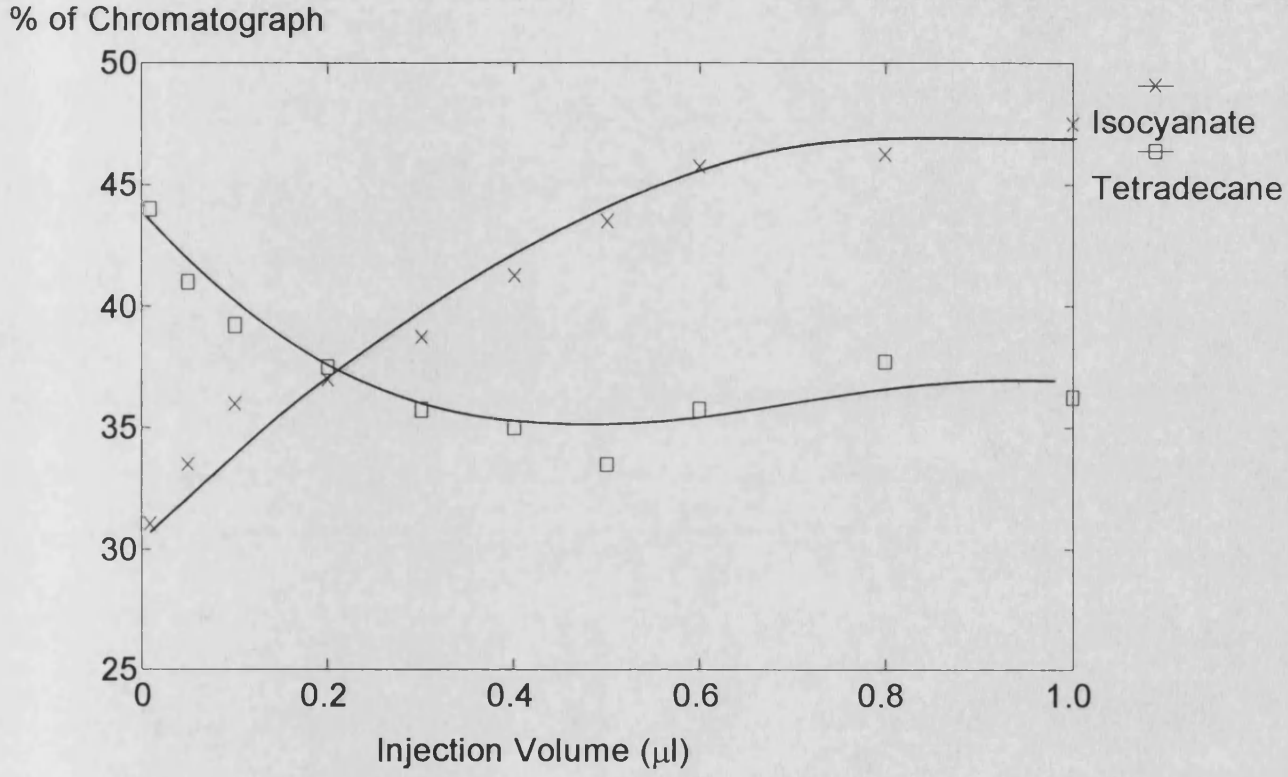
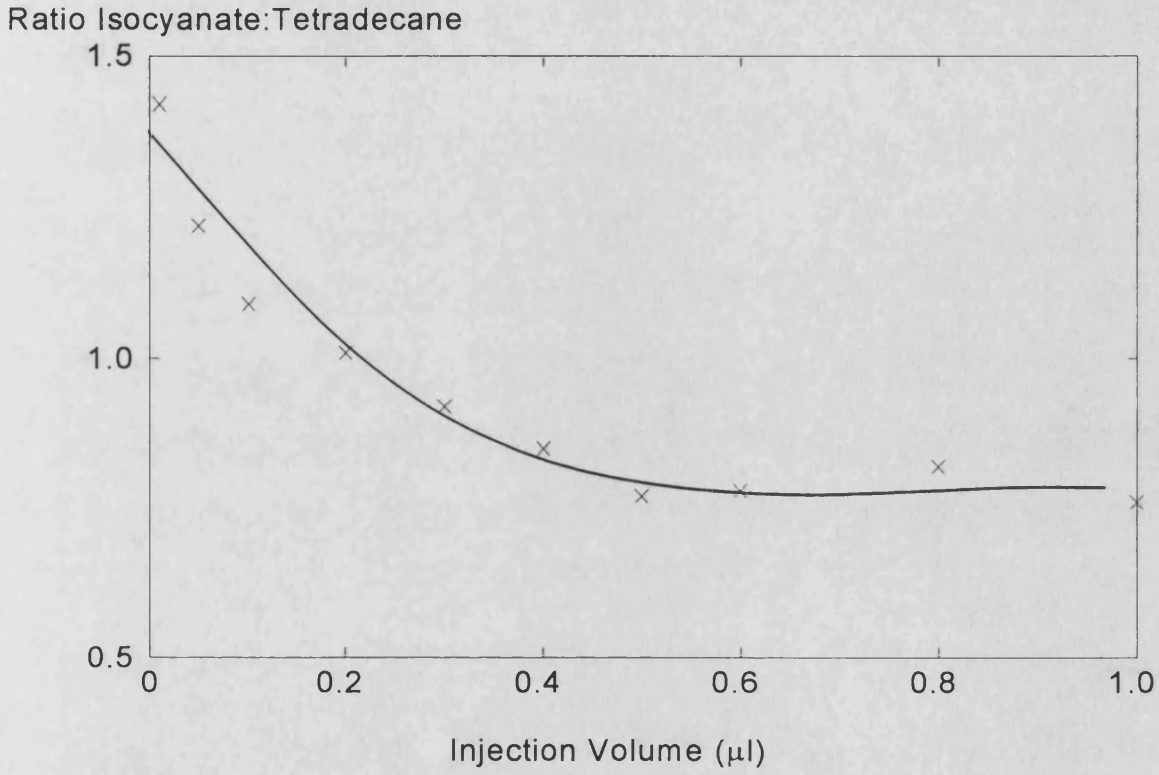


Figure 3.26

Variation of Isocyanate Peak Area:Tetradecane Peak Area with Volume of Sample Injected



this temperature. Experiments were therefore performed at 30°C (equivalent to the ultrasonic heating effect) and samples were removed periodically for G.C. analysis. Each sample was injected 4 or 5 times to allow an average ratio to be obtained.

Initial experiments gave reasonably consistent results, with good agreement between subsequent injections (± 5%). However as the use of the column increased it was found that repeated analyses of the same sample did not agree and that results did not always show a decrease in the isocyanate content of the mixture with time. It is likely that the column was becoming blocked with solid product leading to inefficient separation. Finally, unavailability of the equipment led to the end of further investigations.

Figure 3.27 illustrates the IPDI : tetradecane ratio observed for an ultrasonic reaction with propan-2-ol in heptane and the equivalent stirred reaction. After an "initiation" period of approximately 90 minutes, the proportion of isocyanate in the sonicated experiment fell rapidly. The stirred reaction showed a much more gradual consumption of isocyanate.

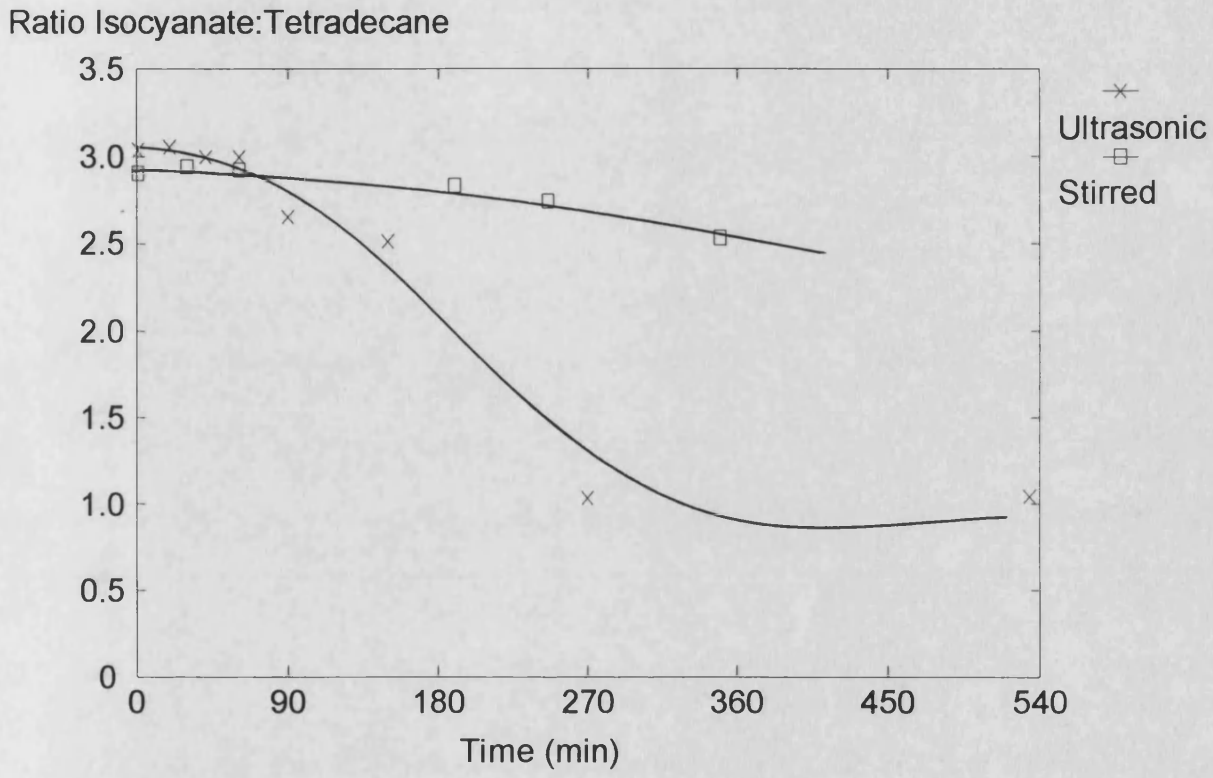
Discussion

The finding of an "initiation" period prior to rapid reaction is consistent with results obtained in the ultrasonic dibutylamine studies (Section 3.3.2). Cunliffe *et al.*[108] in contrast, found that initial G.C. reaction data fitted a second order rate equation. It should be noted however that their experiments were performed at 60°C which could encourage immediate reaction.

Gas chromatography seemed an effective technique for studying the reaction of IPDI and propan-2-ol in solution. It may not be suited to experiments with diols

Figure 3.27

Change in Ratio of IPDI:Tetradecane with time for the Sonicated and Stirred Reactions between IPDI and IPA in hexane



however, where polyurethane production would greatly increase the viscosity of samples for analysis.

3.4 Consideration of Results of Polyurethane Experiments

Comparison of ultrasonic and conventional (heated/stirred) polyurethane reactions has revealed a number of interesting results and opportunities for further study.

Initial experiments showed that ultrasound speeded up reactions between diisocyanates and diols, with polymer sometimes being obtained in one tenth of the time of the equivalent thermal reaction (Table 3.2). More detailed work with the diisocyanate H_{12}MDI corroborated these results and showed that a decrease in reaction time was proportional to an increase in ultrasonic intensity. Ultrasonic reaction products were found to have higher molecular weights than those from thermal or stirred reactions, although molecular weight did not appear to depend on the ultrasonic intensity used. The appearance of ultrasonic products was often found to be different to their conventional equivalents - ultrasound was particularly effective at forming "foamy" materials.

The exact method by which ultrasound leads to the results seen has been discussed (Section 3.2.3). It would appear that enhanced reaction times and molecular weights are likely to be due to a combination of factors (ultrasonic mixing, heating and chemical processes), rather than a single effect. The combined effect may lead to a faster "initiation" of ultrasonic reactions over conventional ones (e.g. the reaching of a specific temperature necessary for reaction).

Difficulties were encountered in devising a technique suitable for studying the kinetics of the polyurethane reactions. To investigate the effects of ultrasound thoroughly, it is desirable to carry out reactions in bulk to prevent any ultrasonic effect on solvents. The nature of the experiments also dictates that a sampling technique be used, rather than *in situ* analysis.

Most of the problems occurring (e.g. in I.R. and dibutylamine experiments) seemed to be due to inhomogeneity of the reaction mixture and hence unrepresentative sampling. Results that were obtained indicated that after an "initiation" period, ultrasonic reactions were rapid. Other workers find that conventional reactions are immediate and follow mainly second order kinetics. However, in most cases harsher reaction conditions were used (reactions that were simply heated or stirred in this study did not "take-off" immediately).

Further work should concentrate on studying the kinetics of ultrasonic reactions to obtain a better understanding of the effects observed. It may be necessary to concentrate on reactions between mono-isocyanates and mono-alcohols, which are more easily analysed, before developing a suitable polyurethane system. A further molecular weight study, using a variety of diisocyanates and diols would also be interesting. Molecular weight can be of extreme importance when producing commercial products.

The next chapter describes the effects of ultrasound on another type of condensation reaction - the ring-opening polymerisation of lactones.

CHAPTER FOUR

ULTRASONIC POLYLACTONE FORMATION

CHAPTER 4

The use of ultrasound to promote ring-opening polymerisations is a relatively new area of research. As described in the introduction (Section 1.5.4), only a few systems have been studied to date.[33,49,50]

The ultrasonically promoted ring-opening of lactones has not been carried out before and was selected for investigation in this study as the resultant ring-opened polyesters have found increasing use as starting materials for agricultural, medical and pharmaceutical applications (Section 1.7.5). Additionally, the similarity in structure between lactones and lactams makes for useful comparisons with work by Ragaini who investigated the ring-opening of ε-caprolactam.[48,49]

Before considering individual experiments, the molecular weight measurement of polylactones in this study will be described.

4.1 Polylactone Molecular Weight Measurement

The determination of molecular weight and polydispersity was an important method of investigating differences between conventional polymers (produced thermally) and those resulting from ultrasonic experiments. All polymers synthesised were analysed by gel permeation chromatography (see Section 2.3.1) and molecular weights reported relative to polystyrene calibration standards. Reproducibility of results was good, with an estimated error of ± 1%.

As discussed in the Introduction (Section 1.2.4), the use of a viscosity detector in a GPC system gives rise to the intrinsic viscosity of a sample under analysis. This in

turn leads to determination of the Mark-Houwink constants, K and α, for the polymer and hence determination of the "true" molecular weight value. In order to find "true" molecular weights in this study, several polyvalerolactone and polycaprolactone samples were analysed by GPC viscometry.

Experimental details are given in Section 2.3.2. Polystyrene standards were analysed first and a calibration graph expressed as log [mol. wt. x intrinsic viscosity] versus elution volume was obtained. When applied to subsequent analysis of polylactones, this gave "true" molecular mass distributions, providing the polymers behaved "normally" in solution.

Table 4.1 gives K and α values as determined for a number of polyvalerolactone and polycaprolactone samples. Each sample was run twice. M_n and M_w values are also shown; the first column gives weights relative to polystyrene whilst the values in parentheses refer to weights calculated from GPC viscosity i.e. "true" values.

The results illustrate that there was a wide variation in K and α values, both between different samples of the same polymer type and sometimes between duplicate runs. There are several possible reasons for this. Firstly, the viscosity detector response increases dramatically with increase in molecular mass, so the technique is not well suited to low molecular mass polymers. The concentration of the polymer is also an important parameter in the calculation and any errors due to insoluble material or non-polymeric soluble impurities will detract form the accuracy of the results. Finally, the added complexity of a second detector tends to hamper reproducibility of results.

Table 4.1

Polylactone Molecular Weights:
Comparison of Polystyrene Equivalent and "True" Values

Sample	Log K	α	M_w		M_n	
			Rel. to PS	"True"	Rel. to PS	"True"
Polyvalerolactone	-2.78	0.47	3410	(2600)	2280	(960)
US, I = 25.4 Wcm^{-2}	-2.86	0.49	3240	(2700)	1800	(1010)
150 min.						
Polyvalerolactone	-3.01	0.54	8000	(6840)	3690	(3690)
Thermal 160°C	-3.04	0.55	8170	(6970)	4730	(3580)
40:1 360 min.						
Polyvalerolactone	-3.13	0.60	7580	(5460)	3900	(2990)
Thermal 150°C	-2.87	0.57	7900	(4870)	3980	(2590)
30:1 480 min.						
Polycaprolactone	-3.42	0.65	5100	(4060)	3890	(3250)
US, I = 18.4 Wcm^{-2}	-3.49	0.68	5190	(4010)	4530	(3510)
60 min.						
Polycaprolactone	-2.98	0.58	7590	(4980)	4740	(3380)
US, I = 18.4 Wcm^{-2}	-3.11	0.61	7500	(5010)	5070	(3380)
105 min.						
Polycaprolactone	-3.35	0.65	9810	(7720)	4130	(5020)
Thermal 150°C	-3.30	0.62	9770	(8170)	5310	(5270)
300 min.						

Rel. to PS = molecular weights relative to polystyrene standards, obtained from conventional GPC.
"True" = molecular weights calculated from GPC viscometry experiments.

Differences in K and α values between individual samples could indicate differences in composition or structure. As all samples were initiated with 1,6-hexanediol and catalysed with dibutyltin dilaurate, differences must arise from the varying polymerisation methods. A long period of sonication appeared to lead to low K and α values for both polyvalerolactone and polycaprolactone. However, these results are by no means clear and a larger number of samples must be tested to establish definite trends.

Schindler[86] studied the uncatalysed ring-opening of ε-caprolactone with 1,6-hexanediol and calculated a log K value of -3.86 and an α value of 0.79. The wide variation observed in the Mark-Houwink constants in this study, makes conversion of relative molecular weights in ultrasonic and thermal experiments to "true" values impractical and all the results following are "polystyrene equivalents". It can be seen however that "true" values of polylactone molecular weights are somewhat lower than polystyrene equivalents.

4.2 General Trends in Lactone Ring-Opening Reactions

The first stage of the study was to perform several experiments to confirm general trends seen in conventional (heated) lactone ring-opening experiments.[81,83] Experimental details for reactions are given in Section 2.2.4.

In order to carry out ring-opening, it is necessary to use some form of initiator and/or catalyst (Section 1.7.2). As already discussed, the term catalyst is often used to describe metal salts added in catalytic quantities in addition to the initiator. However,

such materials sometimes remain as end groups on polymer chains and therefore the description of "catalyst" is not always appropriate.

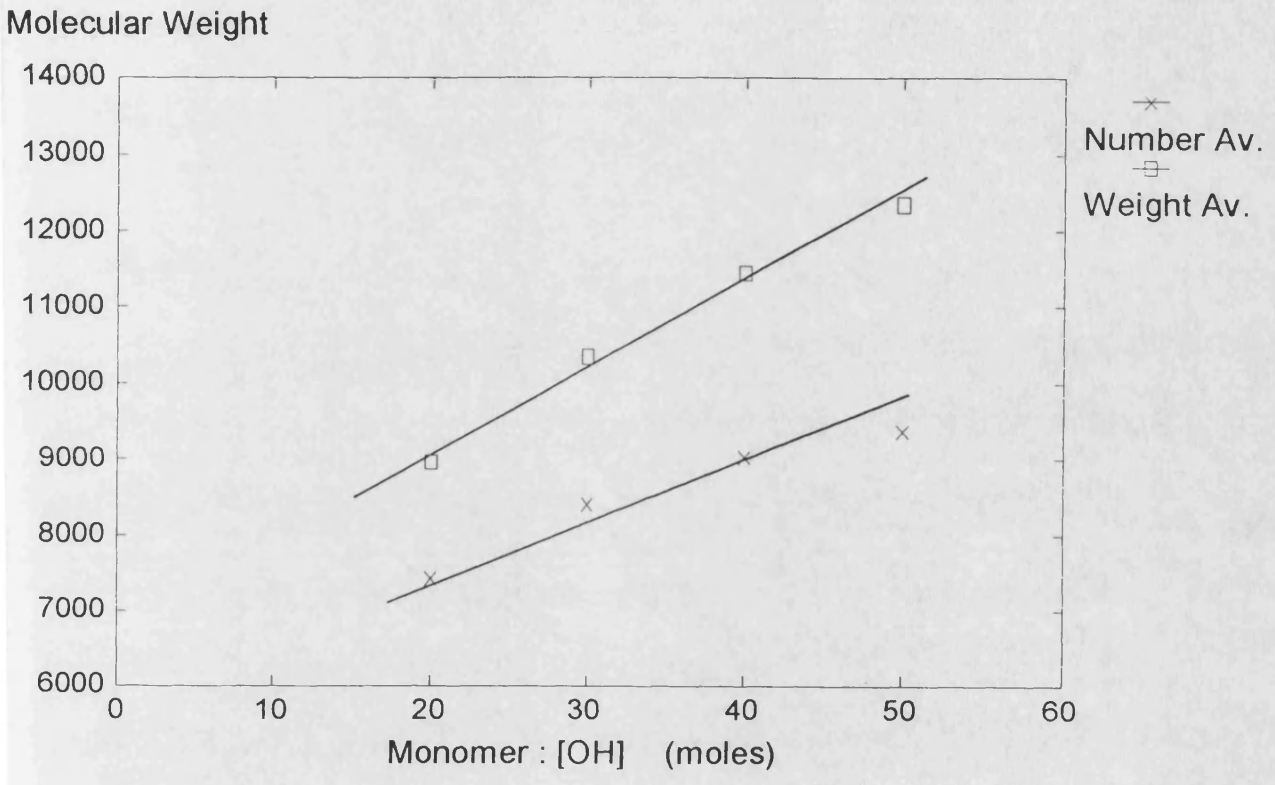
It is known that the molecular weight of the product is dependent on the ratio of the number of moles of lactone to the number of moles of initiator.[110] When initiator concentration is low, the number of sites where chain growth can occur is small, so each polymer chain is long. With a large amount of initiator a greater number of shorter molecules are produced.

To investigate this effect, δ-valerolactone was reacted with the initiator 1,6-hexanediol, using several different [monomer] : [OH] ratios. Experiments were performed in an oven at 160°C for 6 hr and were catalysed with dibutyltin dilaurate(~ 1% by weight). Results are illustrated in Figure 4.1, which shows a linear relationship between molecular weight (M_n and M_w) and the [monomer] : [OH] ratio. It was important therefore that in subsequent experiments, this ratio remained constant. It would otherwise have been impossible to attribute changes in molecular weight to any variation in experimental conditions (e.g. temperature, use of ultrasound). The ratio 30:1 was selected to give reasonably high molecular weights, whilst using a mass of 1,6-hexanediol that was not so small as to give errors in initial weighing of reactants.

As suggested, another important factor in determining polylactone molecular weight at a particular instant during an experiment is the reaction temperature.[79,87] It is usually the case that higher reaction temperatures lead to faster reaction rates. The final molecular weight is determined by the [monomer] : [OH] ratio however and will remain constant whatever the experimental temperature.

Figure 4.1

Effect of [monomer] : [OH] on the Molecular Weight of Polyvalerolactones



This is illustrated in Figure 4.2 which shows the number average molecular weight of polyvalerolactone samples heated for different lengths of time and at different temperatures. Experiments were performed in an oven with a 30:1 [monomer] : [OH] ratio. At 170°C, a reaction time of approximately 2 hr was required to reach the limiting molecular weight of 8500. At 150°C, the reaction time was just under 6 hr.

Accurate control of temperature is therefore important when performing lactone ring-opening experiments.

4.3 Investigation of Polyvalerolactone Formation using Ultrasound

Now that general trends had been established, the study moved to considering a specific system using ultrasound - that of δ-valerolactone. Reactions were performed with 1,6-hexanediol as an initiator, using a [monomer] : [OH] ratio of 30:1, and were catalysed with dibutyltin dilaurate.

The first series of experiments investigated changes in molecular weight with polymerisation time. Reactions were carried out at two temperatures, 150°C and 170°C, and over a range of ultrasonic intensities.

Figures 4.3-4.6 illustrate the change in number average molecular weight (M_n) with time for the four different intensities used. It can be seen that at both temperatures a maximum in molecular weight was reached before the polymer began to degrade. The maximum was reached more quickly at the higher temperature and degradation was more pronounced. Apart from the reaction at 22.1 Wcm^{-2}, experiments at 170°C reached a higher molecular weight before degradation.

Figure 4.2

Effect of Reaction Temperature on the Number Average Molecular Weight of Polyvalerolactones

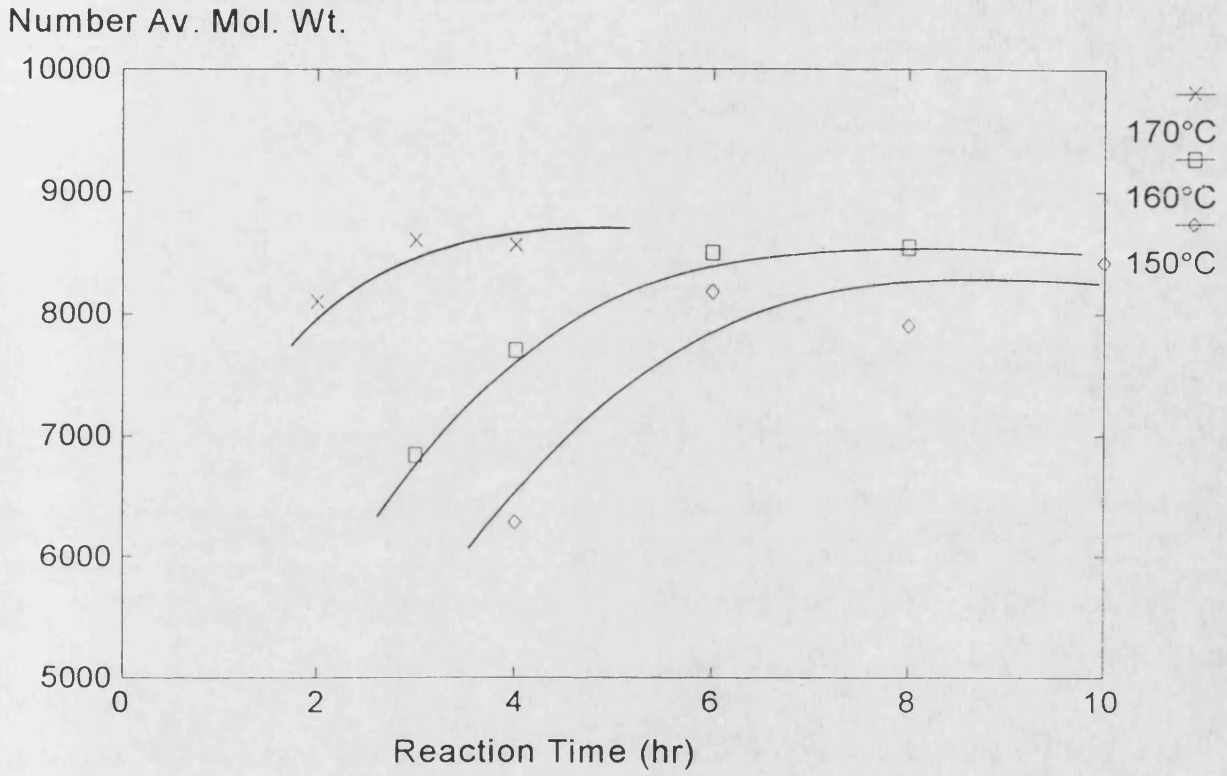


Figure 4.3

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2}

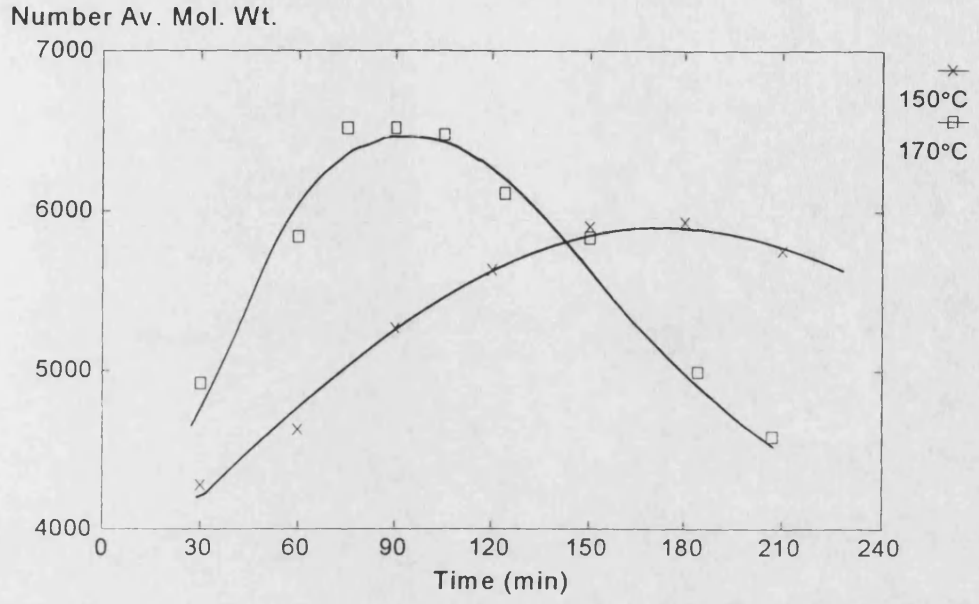


Figure 4.4

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 22.1 Wcm^{-2}

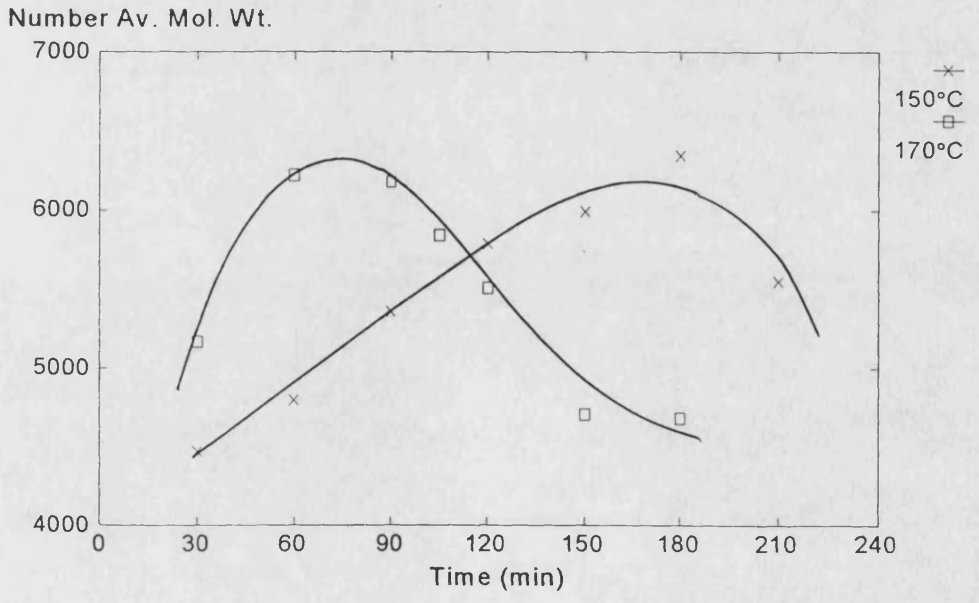


Figure 4.5

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 25.4 Wcm^{-2}

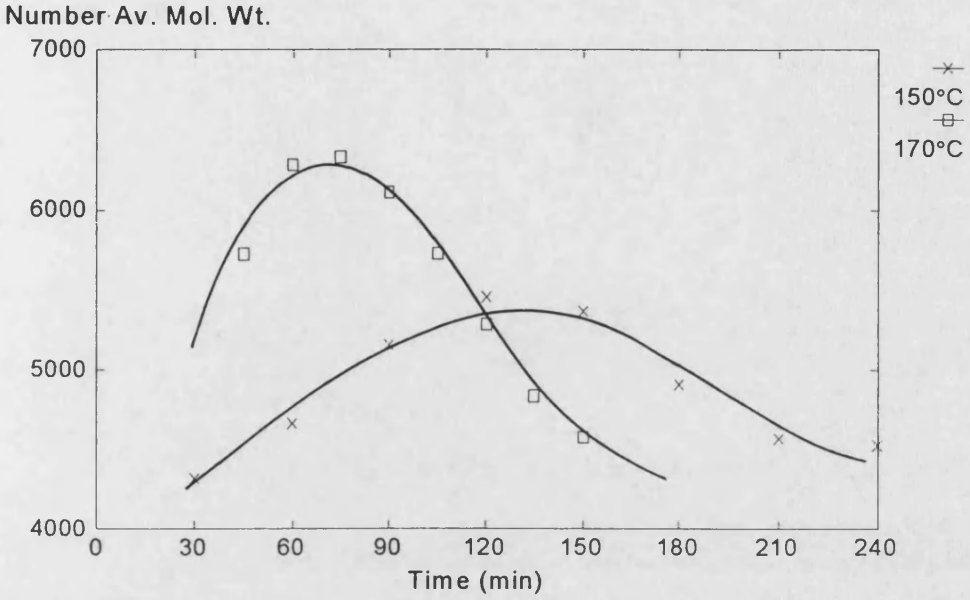
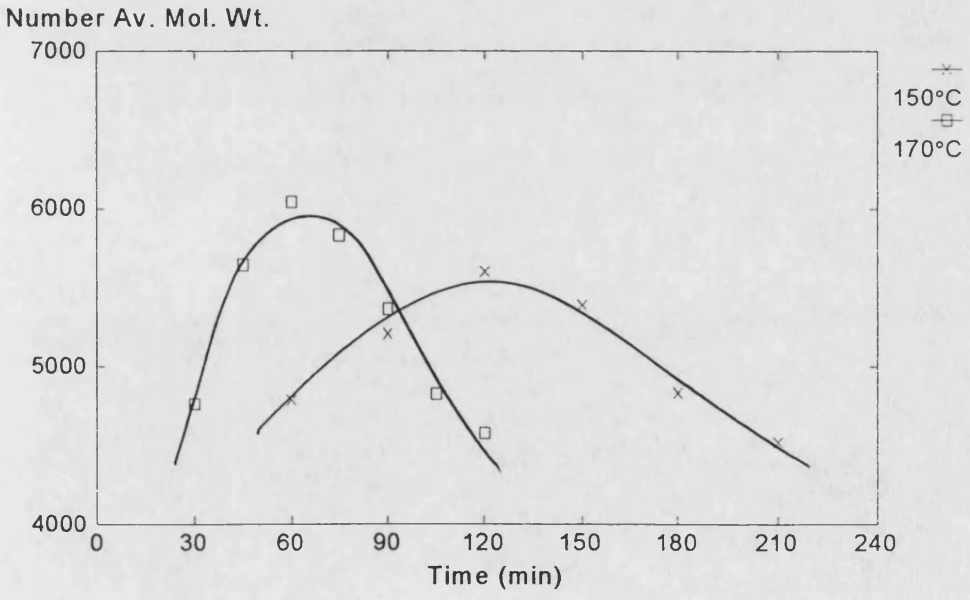


Figure 4.6

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 27.0 Wcm^{-2}



Figures 4.7 and 4.8 give combined results for the 4 different ultrasonic intensities at 150°C and 170°C respectively. Data is also included for the conventional (heated and stirred) reactions at these temperatures.

By examining Figures 4.7 and 4.8 the effects of ultrasonic intensity are made clear. As intensity increased, the time taken to reach the maximum molecular weight decreased and the value of that maximum molecular weight fell. The line representing conventional (thermal) reaction in these graphs illustrated a steady increase in molecular weight with time. At 170°C however, this levelled out upon reaching the limiting molecular weight (8500) determined by the initial [monomer] : [OH] ratio. At the lower temperature of 150°C this limiting weight was not reached in the time scale of the experiment. The graphs also show that there is no evidence of degradation during the reaction.

Figures 4.9-4.12 are the equivalent plots to Figures 4.3-4.6, but this time showing changes in polydispersity with ultrasonic reaction time, The pattern of results obtained was very similar to those in the molecular weight plots. As the molecular weight rose to a maximum at the 4 different intensities, so did the polydispersity. Degradation then caused a narrowing of the molecular weight distribution to give values approaching 1.0. The effects were more pronounced at 170°C.

Figures 4.13 and 4.14. are the equivalent plots to 4.7 and 4.8 (i.e. combined results), but once again give polydispersity data. At higher ultrasonic intensities, maximum polydispersities were reached more quickly and the values of those maximums were lower. In contrast, the polydispersity of the thermally produced polymer increased steadily throughout the reaction.

Figure 4.7

Change in Number Average Molecular Weight with Time for the Thermal and Ultrasonic Polymerisation of δ-Valerolactone at 150°C

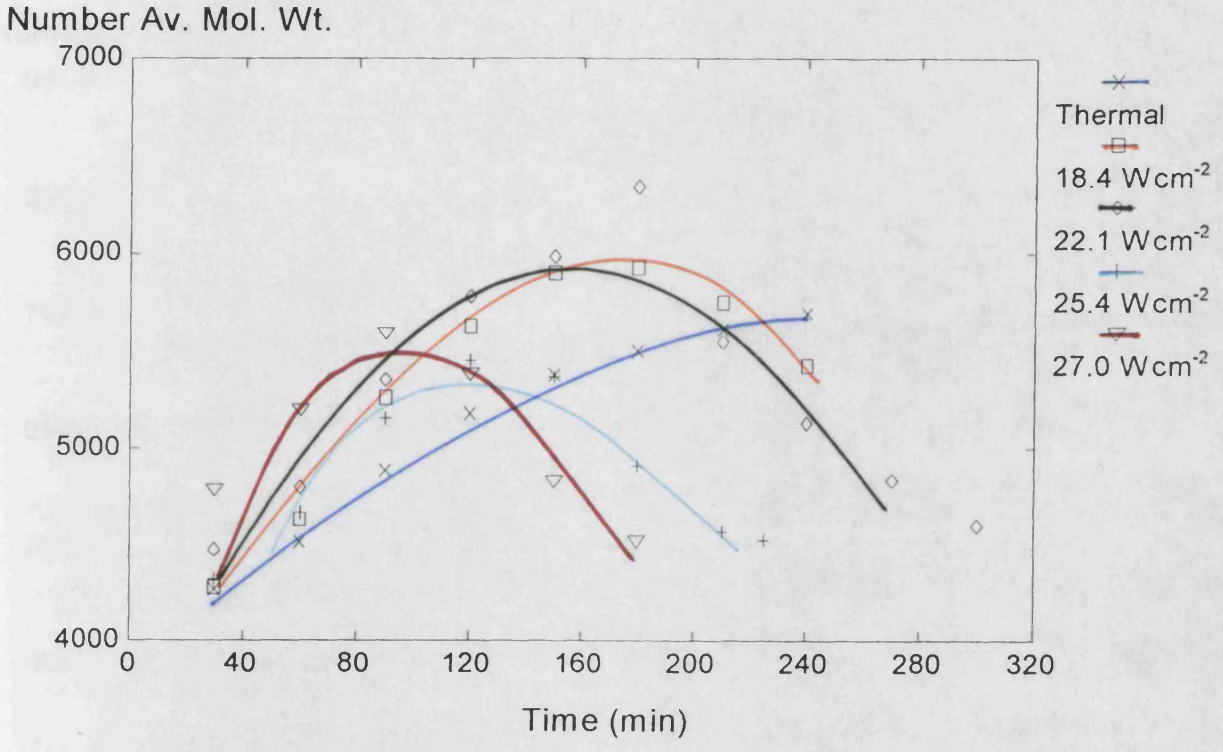


Figure 4.8

Change in Number Average Molecular Weight with Time for the Thermal and Ultrasonic Polymerisation of δ-Valerolactone at 170°C

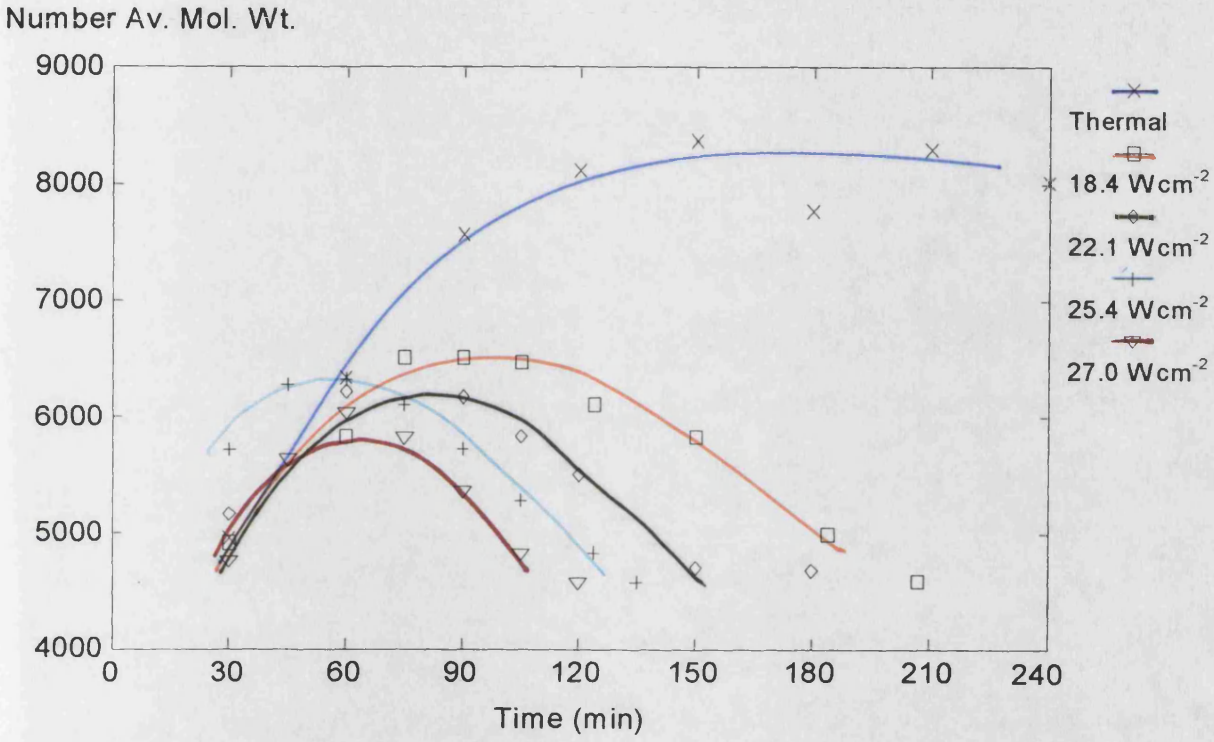


Figure 4.9

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2}

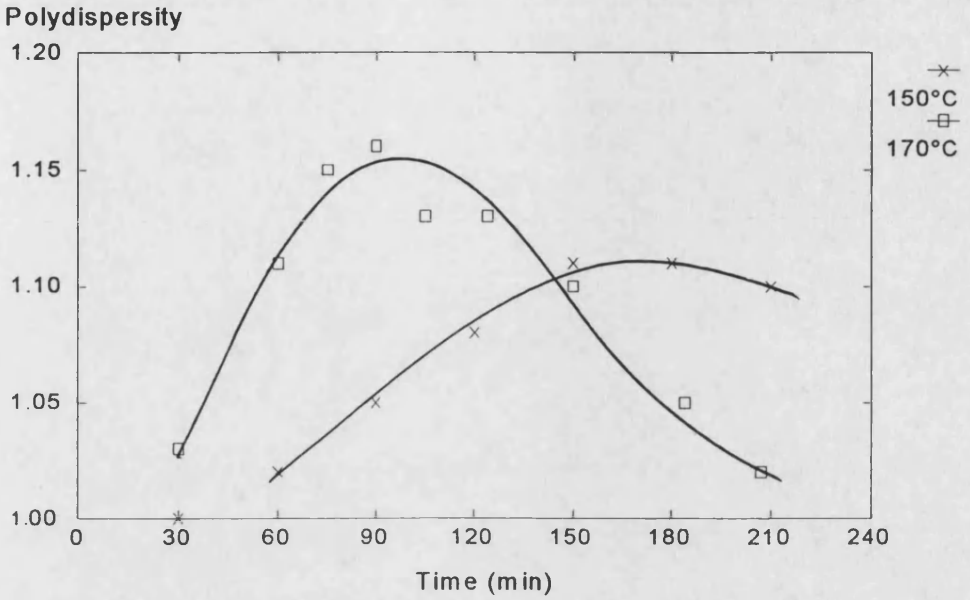


Figure 4.10

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 22.1 Wcm^{-2}

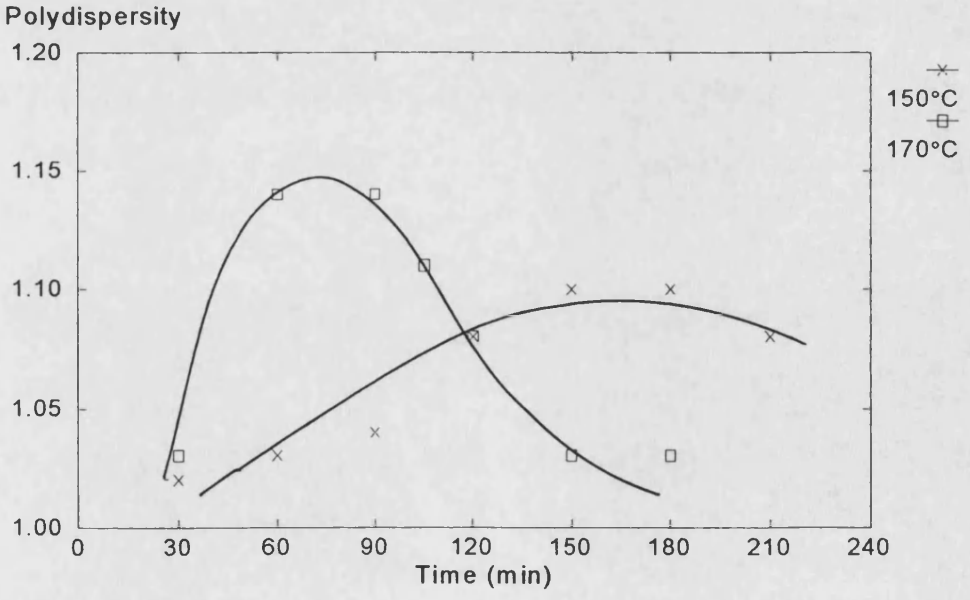


Figure 4.11

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 25.4 Wcm^{-2}

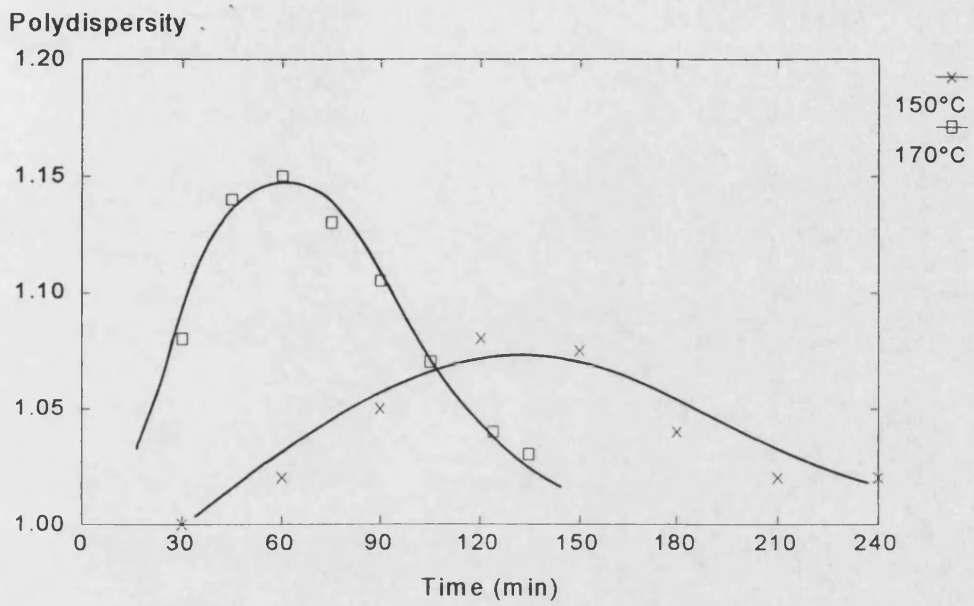


Figure 4.12

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 27.0 Wcm^{-2}

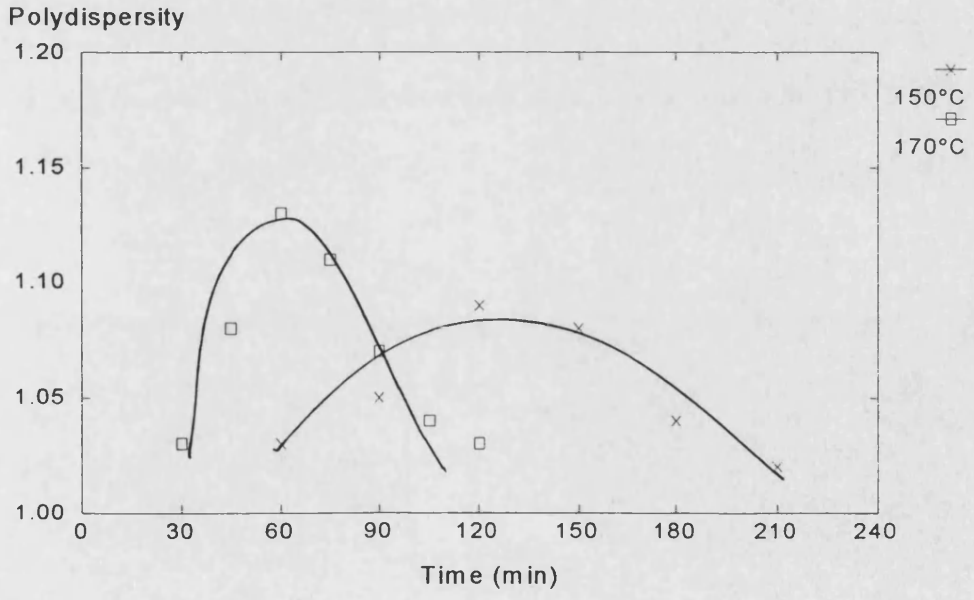


Figure 4.13

Change in Polydispersity with Time for the Thermal and Ultrasonic Polymerisation of δ-Valerolactone at 150°C

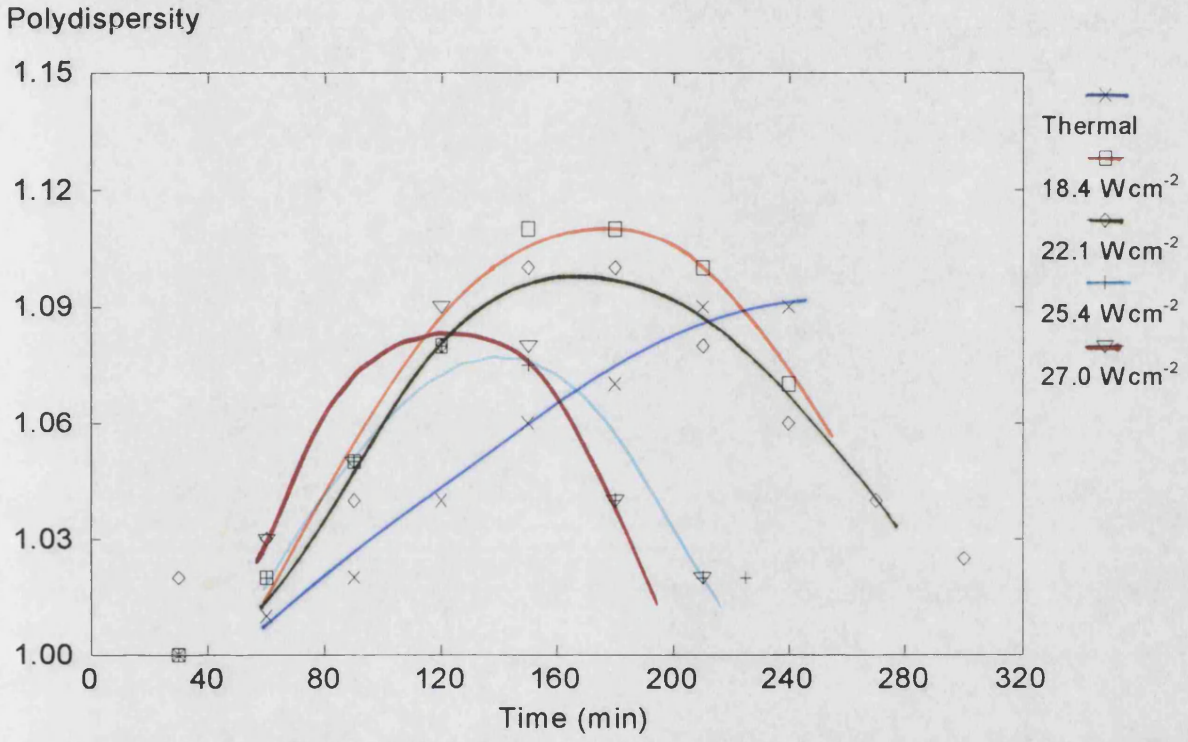
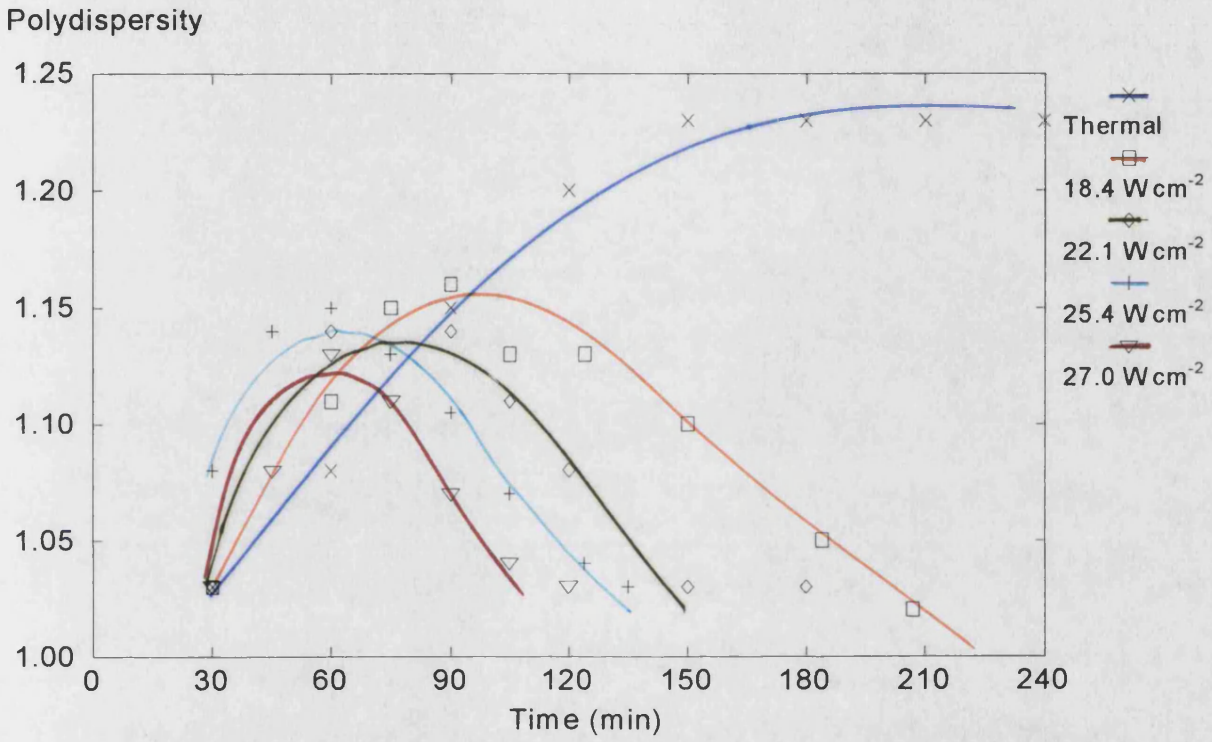


Figure 4.14

Change in Polydispersity with Time for the Thermal and Ultrasonic Polymerisation of δ-Valerolactone at 170°C



Discussion

The two most important effects of ultrasound on the ring-opening polymerisation were the faster formation of polymer in comparison to conventional (heated) reactions and the subsequent degradation of the polymer formed to lower molecular weights.

The ultrasonic enhancement of polymer formation will be considered first. As described in the previous chapter, there are a number of phenomena associated with the sonication of solutions which may explain the effects seen.

δ-valerolactone ring-opening is dependent on effective contact between the monomer and the initiator/catalyst. The violent agitation produced by ultrasound ensures efficient mixing of the reaction components and this will aid faster monomer reaction. As shown in Figure 4.2, the rate of formation of δ-valerolactone is also highly sensitive to reaction temperature. The temperature of the reaction mixture was therefore continually adjusted to allow for ultrasonic heating effects.

As cavitation bubbles implode, violent shock waves are generated which can expose δ-valerolactone rings to large shear forces. Any resultant acyl-oxygen or alkyl-oxygen cleavage would give rise to reactive ring-opened species, able to join a growing polymer chain or to initiate further ring-opening.

Figures 4.7 and 4.8 show that during polyvalerolactone formation, polymer molecular weight was dependent on the ultrasonic intensity used. This is in contrast to results obtained during sonochemical polyurethane experiments where no link was found, although ultrasonically produced polymers did have higher molecular weights than their conventional equivalents. In the case of the δ-valerolactone polymer, the

greater stirring and cavitation effects at higher intensities must have been responsible for the increase in molecular weight seen.

There have been only a few past studies of ultrasonically promoted ring-opening reactions (Section 1.5.4) and little discussion of the role that ultrasound plays. Ragaini[48,49] was able to ring-open ε-caprolactam using ultrasound without the addition of water (the usual initiator). As no other reaction components were present, this suggests that ultrasound was able to cleave the ring (e.g. by means of shear forces or heating) to give a reactive monomer.

Stoessel[50] used ultrasound in the ring-opening of polycarbonate oligomers (see also Section 1.5.4). He attributed polymerisation to high local cavitation temperatures, or to the sonochemical initiation of an anionic process, promoted by trace impurities (e.g. sodium hydroxide).

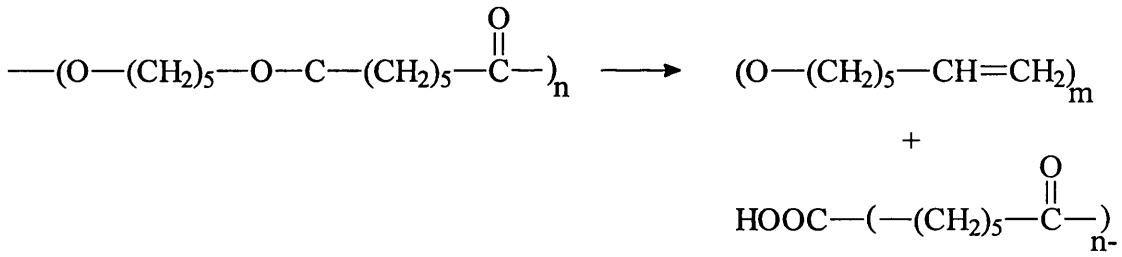
It would seem that a far greater number of studies are needed to isolate the precise role which ultrasound plays in promoting ring-opening.

Attention will now turn to the polymer degradation observed during reaction. As discussed in the introduction (Section 1.5.2), ultrasonic degradation is a well documented phenomena and several mechanisms have been proposed to explain its occurrence.

While most workers agree that degradation is a result of cavitation, the particular cavitational effect responsible has been debated. Possibilities studied have been; (i) thermal effects due to the hot spots created in bubbles, (ii) shock waves produced form transient bubble collapse and (iii) shear forces from pulsating stable cavitations[2] (for a fuller discussion see 1.5.2).

Many studies have concentrated on the degradation of high molecular weight polymers in solution.[33,111] It is usually found that a limiting molecular weight exists, often several tens of thousand, below which no further degradation occurs.[112,113]

The polyvalerolactones of this study were of far lower molecular weight (M_n typically 6500 relative to polystyrene), yet degradation occurred readily. It should also be noted that reactions were performed in bulk, so degradation theories relating to solvent effects are not likely to be applicable. It is known that in thermal experiments involving polylactones, thermolysis (e.g. cleavage of the ester linkages in the chain) can take place. Rafler,[29] in experiments with ε-caprolactone found that depolymerisation began to occur after approximately 10 hr at 150°C. The cleavage reaction led to the formation of carboxylic groups and unsaturated compounds.



Saotome[110] reported that polyvalerolactone initiated with ethylene glycol showed substantial weight losses after being heated at 200°C.

It seems probable therefore, that ultrasound accelerated a thermally-based form of degradation in the experiments in this study. The relatively short length of the polymer chains would suggest that a mechanism involving cavitational shear forces and resulting in centre cleavage of chains was less likely.

During ultrasonic experiments, both polymerisation and depolymerisation

reactions would have been competing with each other. This was illustrated in Figures 4.7 and 4.8, which show that the maximum molecular weights achieved decreased as ultrasonic intensity increased i.e. at higher intensities the effects of degradation became more pronounced.

The ultrasonic degradation of polymers can be complicated and a number of workers have attempted to define a rate equation for the process.[114-116] Factors considered when formulating kinetic models have included polydispersity, solution concentration and degree of polymerisation. In order to investigate the degradation observed during polymerisation reactions in the current study, first-order rate data was calculated for the experiments illustrated in Figures 4.7 and 4.8. This is illustrated in Figure 4.15.

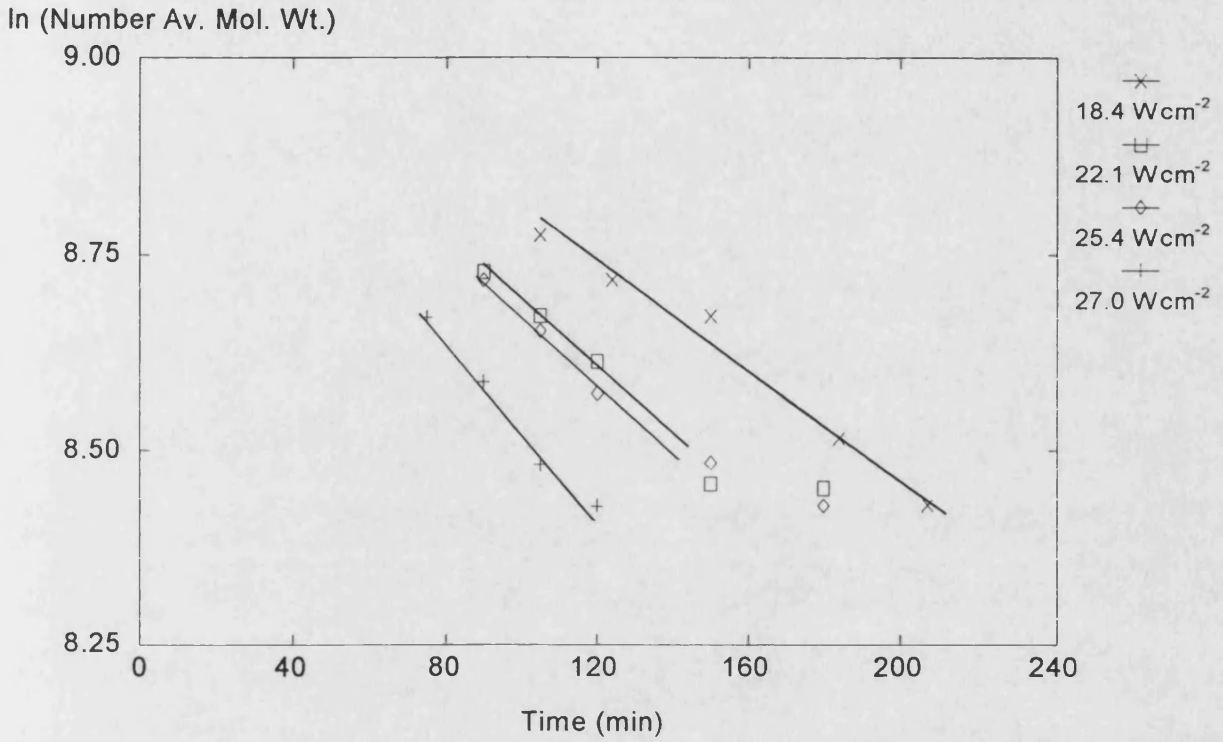
Although only a few data points were collected for each reaction, good linear plots were obtained, in particular for the initial phase of the degradation. The simplest model proposed by Xu[115] for ultrasonic solution degradation was also a first-order model. In a thorough study by Smith however,[35] it was found to give a poor description of the degradation occurring when polystyrene was sonicated in a variety of solvents. This supports the theory that the type of degradation seen during ultrasonic formation of polyvalerolactones is very different from the conventional degradation of longer chain molecules in solution.

4.4 Investigation of Polycaprolactone Formation using Ultrasound

As a comparison with reactions involving δ-valerolactone, the ring-opening polymerisation of ε-caprolactone was briefly investigated. A 30:1 ratio of lactone to

Figure 4.15

Rate of Degradation of Polyvalerolactone during Polymer Formation at 170°C



1,6-hexanediol was used and reactions were performed thermally and ultrasonically at150°C, using dibutyltin dilaurate as a catalyst. Molecular weight and polydispersity results are given in Figures 4.16 and 4.17.

The ultrasonic reaction proceeded faster than the thermal/stirred experiment and the molecular weight distribution of the resultant polymer was higher. After approximately 150 min, the sonicated experiment became too viscous to support cavitation and it was necessary to stop the reaction. Ultrasonic degradation, characteristic of the polyvalerolactone experiments was not observed.

These results support findings by other workers investigating conventional ring-opening of lactones. Storey[82] describes how the reversibility of a polymerisation. especially under conditions where a high equilibrium monomer concentration ($[M_c]$) exists, can greatly effect the resulting molecular weight. Because of differing $[M_c]$'s, the homopolymerisations of δ-valerolactone and ε-caprolactone behave differently. The polymerisation of δ-valerolactone initiated by ethylene glycol at 160°C led to only low molecular weight polymer with substantial amounts of monomer remaining.[81] ε-caprolactone however, was found to be converted almost quantitatively to high molecular weight polymer under the same conditions.[86]

The lower $[M_c]$ of the polycaprolactone system makes it less prone to thermal and hence to ultrasonic degradation i.e. the monomer-polymer equilibrium favours the formation of polymer.

Figure 4.16

Change in Number Average Molecular Weight with Time for the Thermal and Ultrasonic (18.4 Wcm^{-2}) Polymerisation of ε-Caprolactone

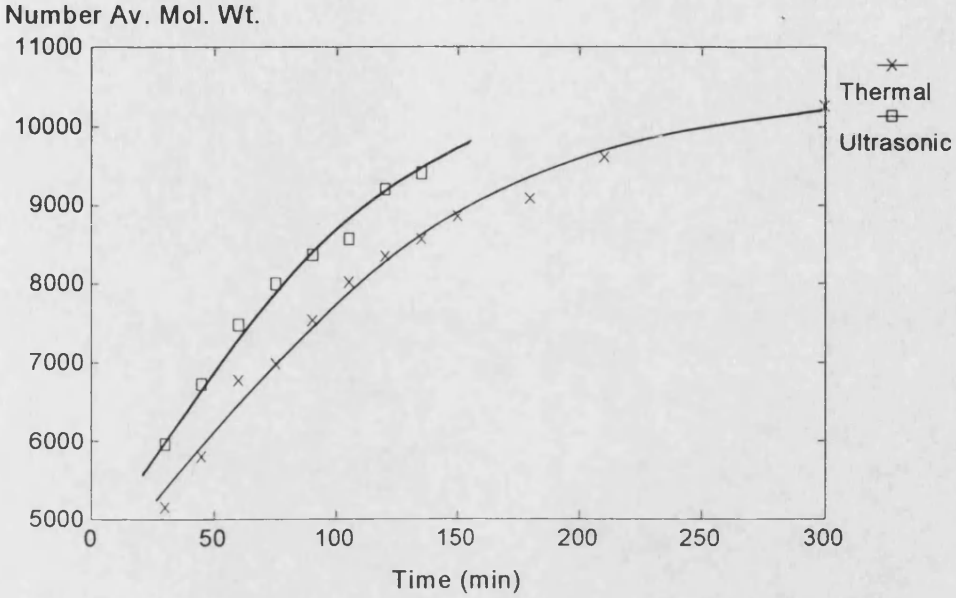
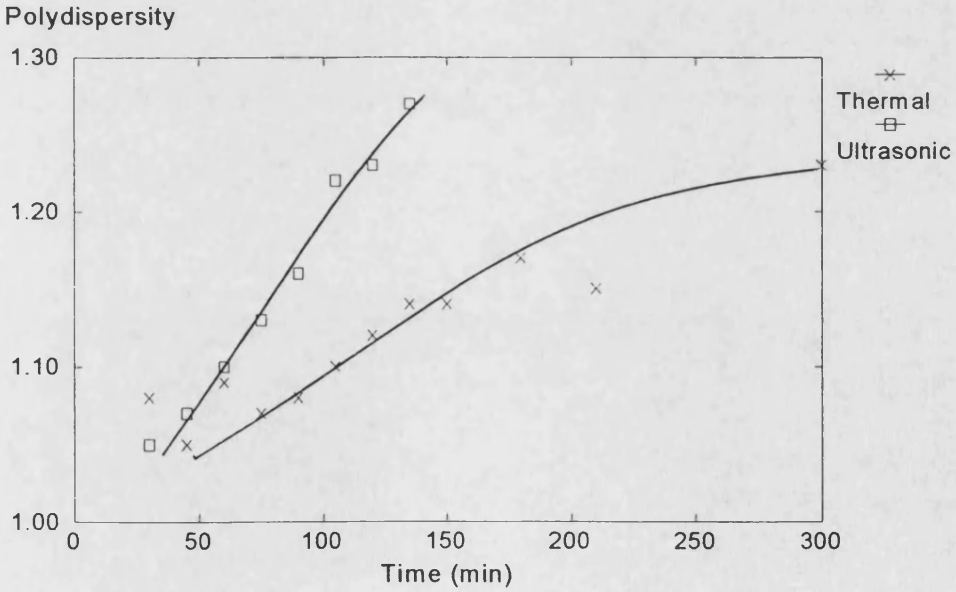


Figure 4.17

Change in Polydispersity with Time for the Thermal and Ultrasonic (18.4 Wcm^{-2}) Polymerisation of ε-Caprolactone



4.5 Effect of Catalyst and Initiator on the Ultrasonic Ring-Opening of δ-Valerolactone

All experiments so far described in the study used both an initiator (1,6-hexanediol) and a catalyst (dibutyltin dilaurate) to promote polymerisation. It was decided to investigate the effect of omitting one or both of these components. Both thermal and ultrasonic (18.4 Wcm^{-2}) experiments were carried out at a reaction temperature of 150°C.

Catalyst Present, No Initiator

Figures 4.18 and 4.19 illustrate molecular weight and polydispersity data for the ultrasonic reaction using only δ-valerolactone and dibutyltin dilaurate. For comparison, the equivalent plot for the reaction with both initiator and catalyst is also shown (from experiments performed in section 4.3).

Figures 4.20 and 4.21 give results for the thermal reaction and once again include data for the equivalent reaction containing both catalyst and initiator. It should be noted that the uninitiated thermal reaction gave broad GPC traces showing a large amount of unreacted monomer. The molecular weight data obtained for the first 4 points is therefore at best an approximation of the higher molecular weight material in the sample. This is illustrated in Figure 4.22 which is a comparison of an uninitiated ultrasonic and an uninitiated thermal GPC plot after 2 hours of reaction.

The graphs illustrate a number of points. Firstly, ultrasonic ring-opening was initiated by the catalyst alone and the molecular weight of the polymer was higher than in a system additionally containing 1,6-hexanediol. This is to be expected, as the fewer

Figure 4.18

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} without Initiator

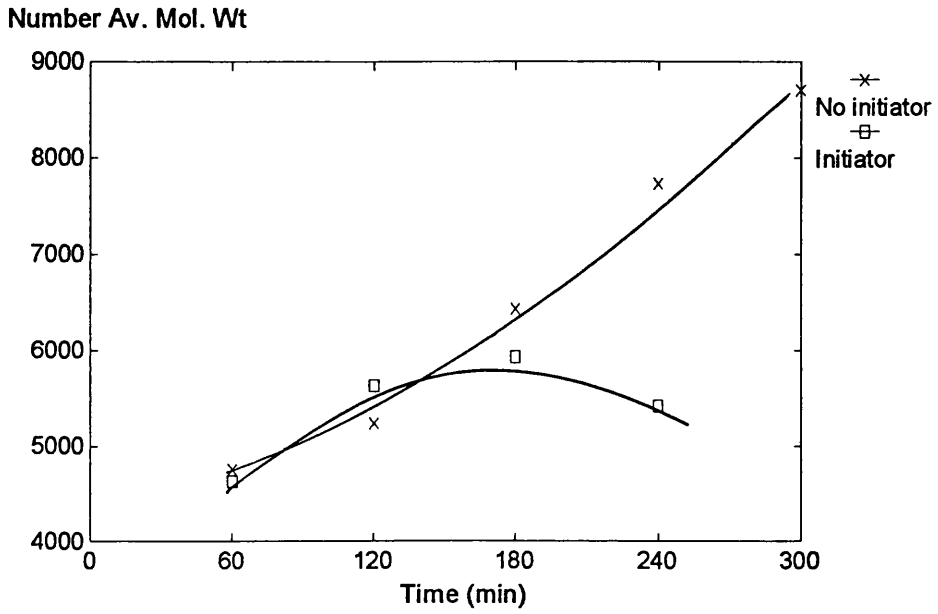


Figure 4.19

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} without Initiator

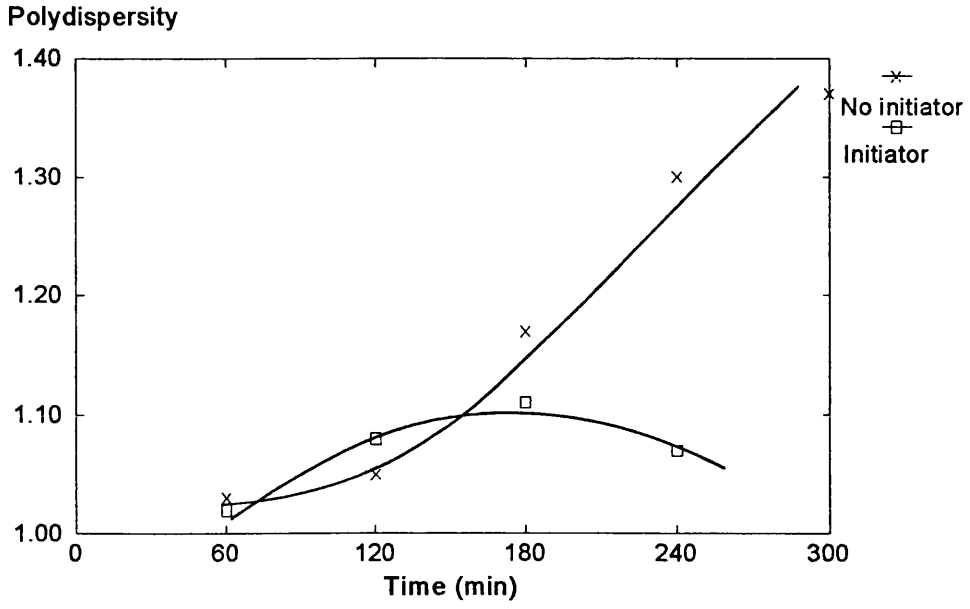


Figure 4.20

Change in Number Average Molecular Weight with Time for the Thermal Polymerisation of δ-Valerolactone without Initiator

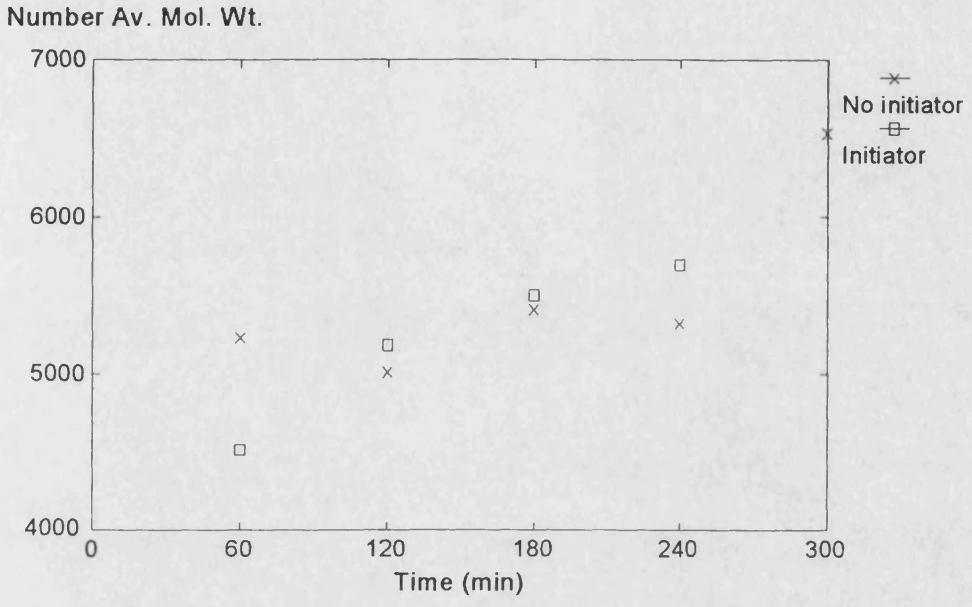


Figure 4.21

Change in Polydispersity with Time for the Thermal Polymerisation of δ-Valerolactone without Initiator

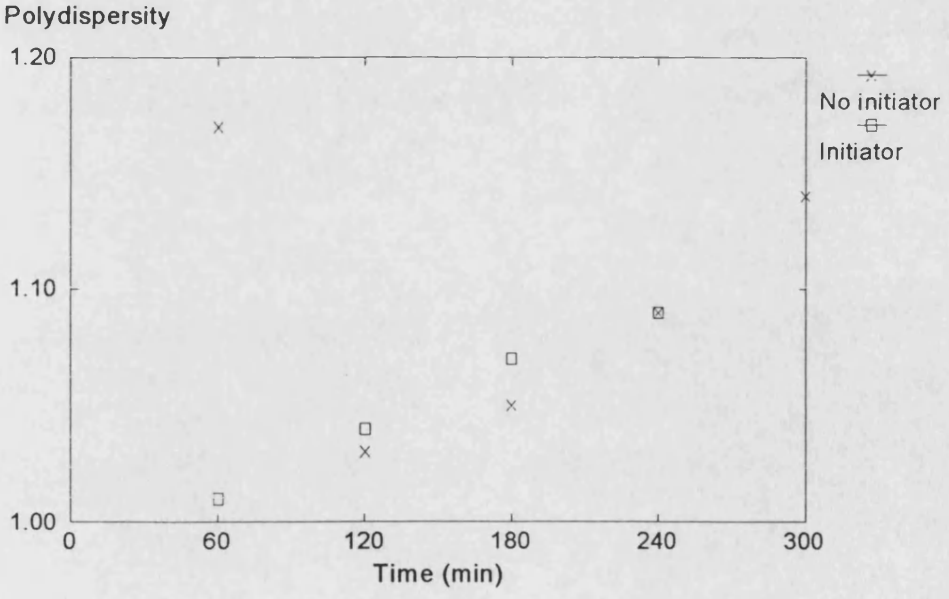


Figure 4.22a

Gel Permeation Chromatogram of a Polyvalerolactone Sample produced without Initiator and using Ultrasound at 18.4 Wcm^{-2}

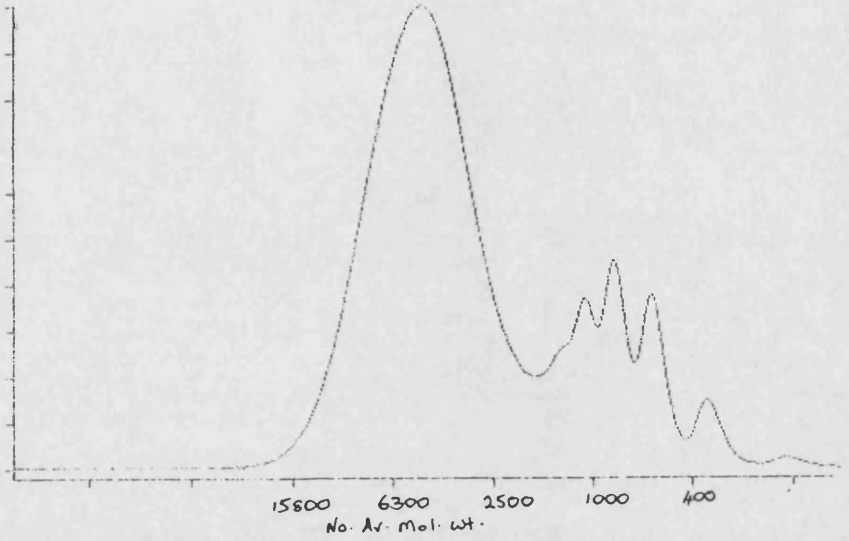
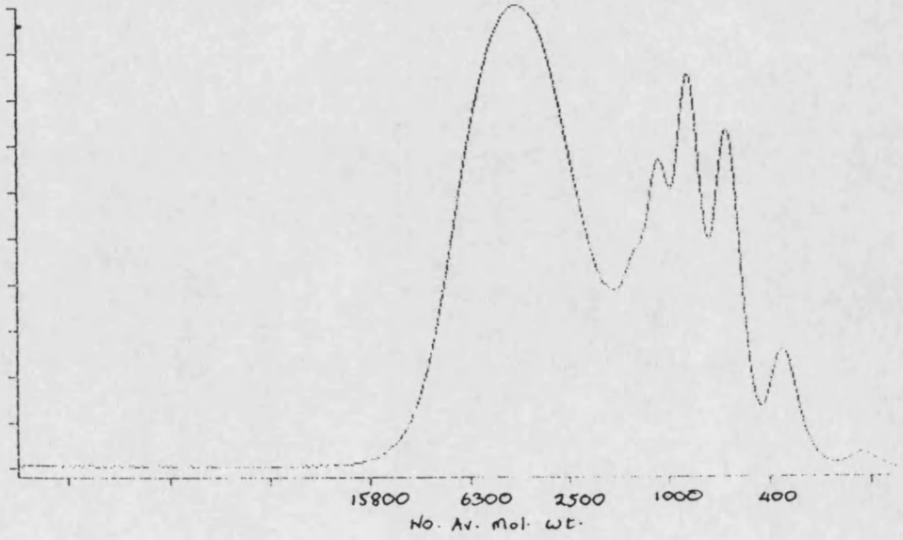


Figure 4.22b

Gel Permeation Chromatogram of a Polyvalerolactone Sample produced thermally without Initiator



the initiating sites, the longer the chain growth at each individual site. It is interesting that no ultrasonic degradation was observed in the uninitiated system. It could be that degradation is occurring, but that the competing polymerisation reaction masks the effect.

In the time period of the experiment, uninitiated thermal polymerisation did not result in high molecular weight polymer, as illustrated by the GPC trace. Ultrasound was far more effective at promoting reaction. Results will be discussed further at the end of this section.

Initiator Present, No Catalyst

Figures 4.23 and 4.24 give molecular weight and polydispersity results for ultrasonic experiments using 1,6-hexanediol, but no catalyst. The equivalent ultrasonic reaction with both catalyst and initiator is shown for comparison.

Figures 4.25 and 4.26 give the corresponding thermal results. As in the previous system, very broad GPC peaks were obtained from samples for the first 4 hours of the thermal experiment, due to the presence of a large amount of low molecular weight material.

The graphs show that although some low molecular weight polymer was produced in the absence of catalyst, in neither the thermal or ultrasonic reactions did the molecular weight of the samples appear to increase. Polydispersities were extremely low (cf. the previous system which contained catalyst but no initiator).

Figure 4.23

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} without Catalyst

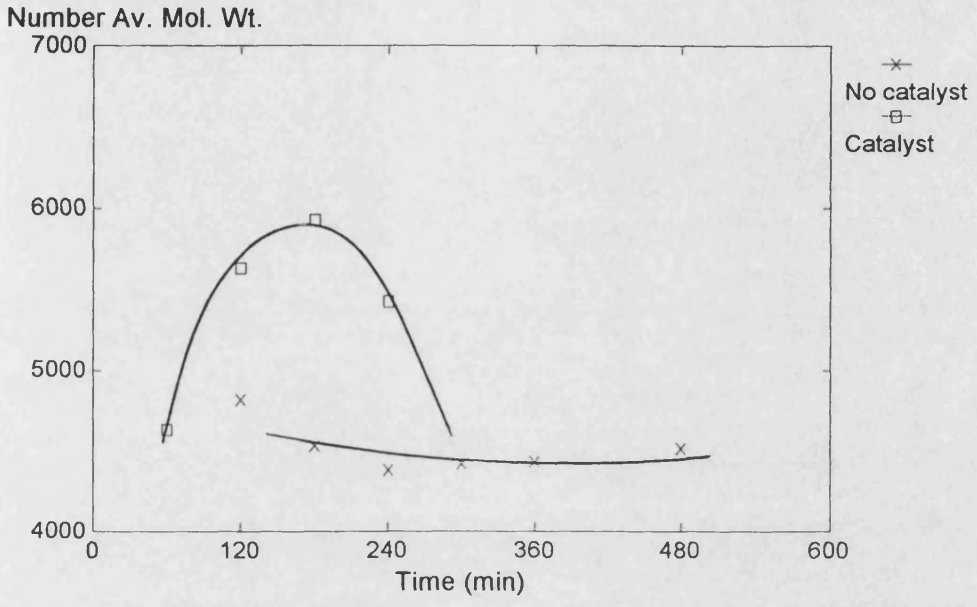


Figure 4.24

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} without Catalyst

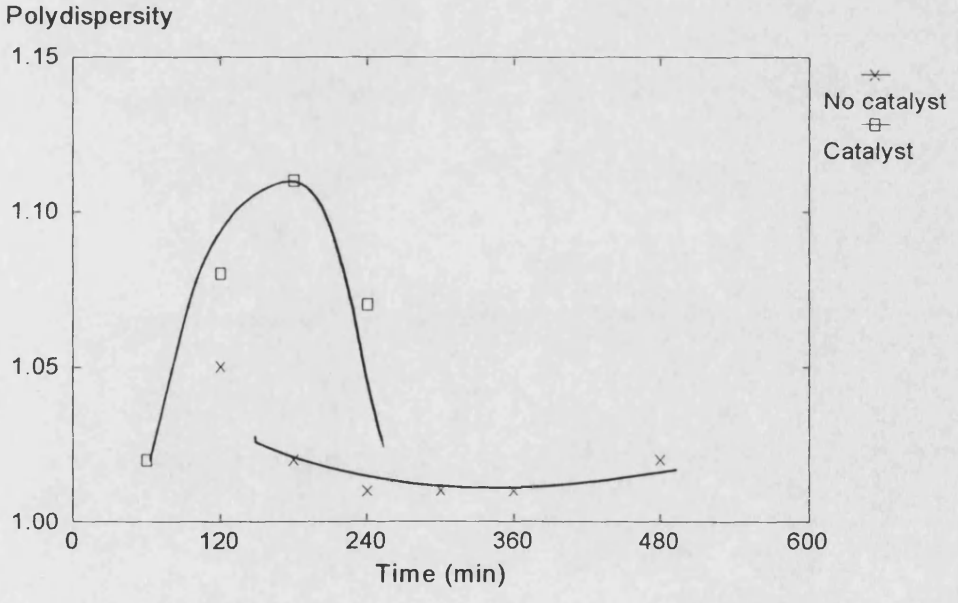


Figure 4.25

Change in Number Average Molecular Weight with Time for the Thermal Polymerisation of δ-Valerolactone without Catalyst

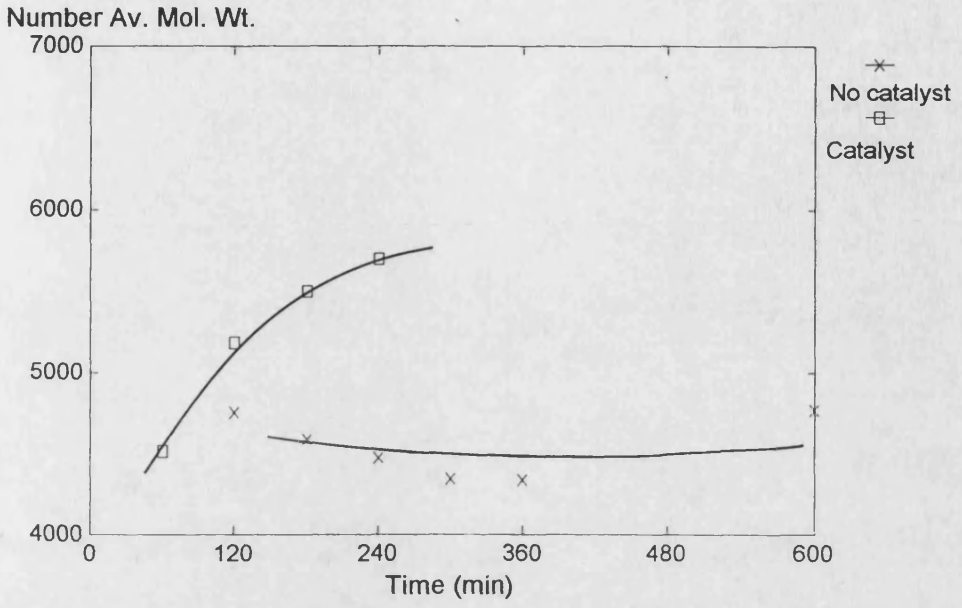
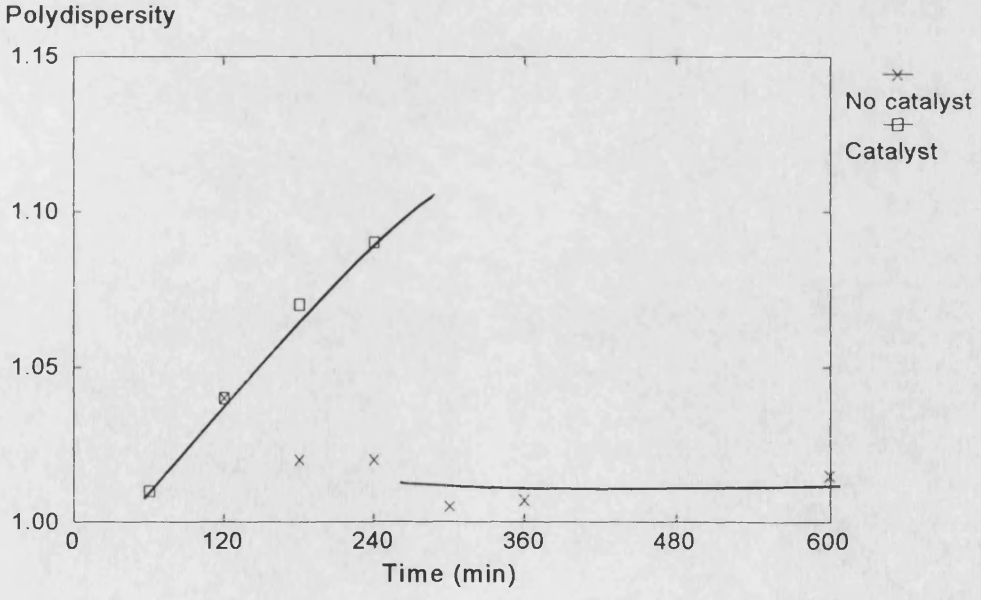


Figure 4.26

Change in Polydispersity with Time for the Thermal Polymerisation of δ-Valerolactone without Catalyst



The use of initiator alone therefore, resulted in low molecular weight material with a very uniform chain length. Ultrasound gave no apparent advantage over the thermal reaction (apart from a faster formation of polymer).

No Catalyst Present, No Initiator Present

Figures 4.27 and 4.28 illustrate results for ultrasonic polymerisation of δ-valerolactone with no catalyst or initiator present. There is no graph showing results from thermal experiments performed in the same way, as it was impossible to identify a polymer peak on the GPC traces.

The results show that some degree of polymerisation occurred in the ultrasonic system, but molecular weights appeared to reach a constant level. There was no evidence of ultrasonic degradation. No polymer was produced in thermal experiments within the time-scale of the experiment.

Discussion

The omission of components from the reaction mixture produced a number of interesting results and the three experiments performed will be considered in turn.

The ultrasonic production of polymer using dibutyltin dilaurate alone supported the findings of other workers in the ability of tin salts to act as initiators in the absence of hydroxy-compounds. Rafler[79] reacted ε-caprolactone with a number of tin (II) carboxylates and tin (II, IV) halogenides. Molecular weight depended on such factors as temperature and tin salt concentration. Tin (II) octoate was the most effective initiator and Rafler proposed a mechanism for its ring-opening action:

Figure 4.27

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} with neither Catalyst nor Initiator

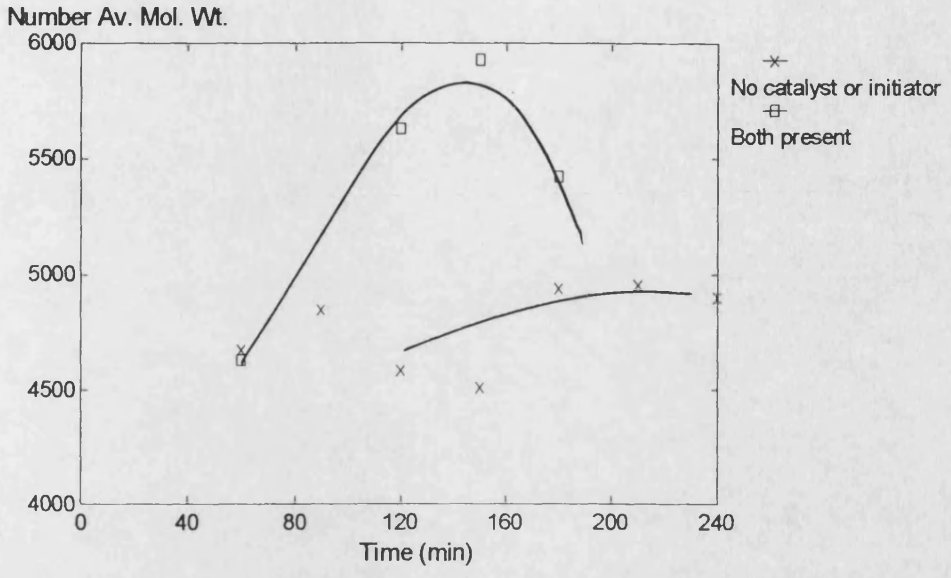
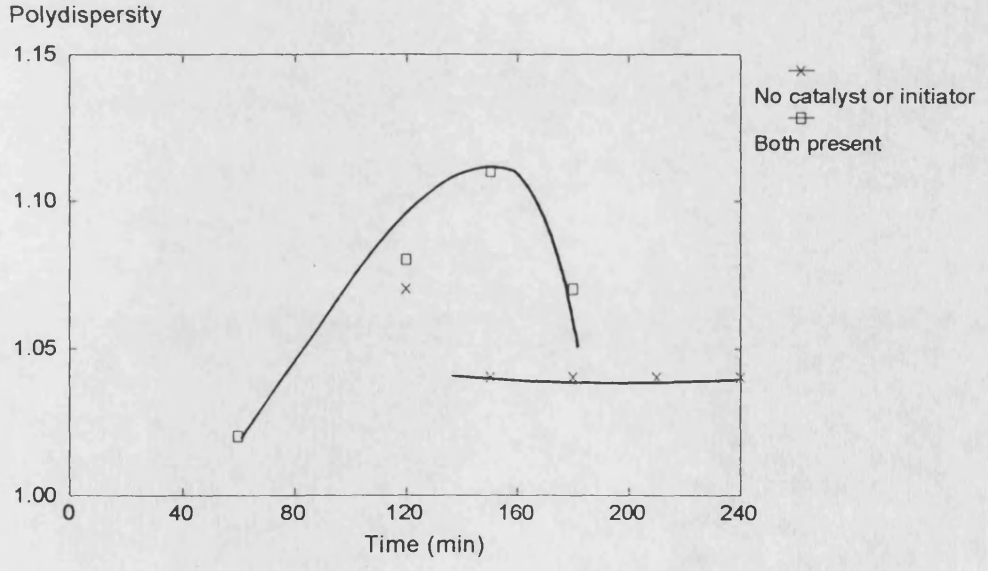
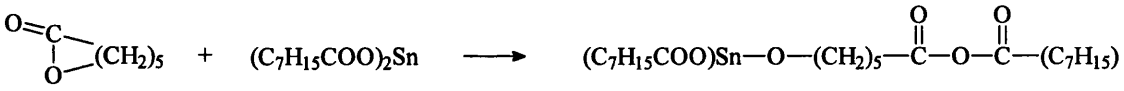


Figure 4.28

Change in Polydispersity with Time for theUltrasonic Polymerisation of δ-Valerolactone at 18.4 Wcm^{-2} with neither Catalyst nor Initiator





He found that when high concentrations of initiator were present, depolymerisation of the caprolactone polymer occurred as the reaction progessed. This may explain why the ultrasonic experiment using only dibutyltin dilaurate gave rise to higher molecular weight polymer than that additionally containing 1,6-hexanediol (Figure 4.18). When only a small concentration of initiating species was present, fewer concurrent reactions leading to degradation occurred (e.g. interchange reactions and thermolysis), and fewer sites for chain growth existed, giving longer chains at each site.

As discussed in the Introduction (Section 1.7.4), there is some debate as to the role of tin salts in lactone ring-opening. Schindler,[86] in contrast to Rafler found little polymerisation in ε-caprolactone containing only stannous octoate and suggested that this was due to residual water in the monomer. Gorda[87] has suggested that the role of the catalyst is to promote the reaction of a hydroxy-terminated ring-opened monomer with another molecule.

Whatever the exact mechanism of action, there is no doubt that ultrasound promotes polymerisation more effectively than the use of heat alone (Figure 4.18 cf. Figure 4.20). This could be a result of any number of the factors discussed in Section 4.4, namely; more ready acyl/oxygen and alkyl/oxygen bond cleavage, improved dispersal of the tin salt and localised heating effects.

The ultrasonic and thermal initiation of δ-valerolactone using 1,6-hexanediol only produced low molecular weight material with a very low polydispersity (Figures

4.23 and 4.25). It is known from initial experiments that the diol is an important reaction component, with the [monomer] : [OH] ratio determining final molecular weight (Figure 4.1). The failure of the diol to cause effective polymerisation in the absence of dibutyltin dilaurate underlines the importance of the tin salt in the reaction process.

It is suggested that the most appropriate theory to describe the current system is one combining that of Gorda[87] and Schindler[86] i.e. ring-opening is initiated by 1,6-hexanediol (or in its absence by residual water) and the propagation step is catalysed by the tin salt. This would explain the lack of polymer growth when catalyst was absent.

The theory is corroborated by the result of the final experiment in the series (no catalyst or initiator in the reaction mixture). Figure 4.27 shows molecular weights obtained for the ultrasonic experiment. It can be seen that, as with the experiment using diol alone, only low molecular weight polymer was produced. This can be attributed to ring-opening by residual water in the monomer.

In both the experiment using initiator only and that with neither initiator or catalyst, ultrasound was more efficient at ring-opening than the use of heat alone. This was especially true in the latter experiment, where it was not possible to isolate polymer peaks in the gel permeation chromatographs of thermal samples. Ultrasound must therefore promote the action of hydroxyl compounds (diols or residual water) through a variety of cavitation effects.

4.6 Solution Polymerisation of δ-Valerolactone

A brief investigation was made of the feasibility of performing ultrasonic lactone ring-opening reactions in solution. As discussed in the introduction (Section 1.5.3), ultrasonic free radical polymerisations occur readily in solution. In this study, difficulty lay in selecting a solvent that would not initiate ring-opening and that also had a boiling point well above the reaction temperature.

Initial experiments used 1,4-dioxane (b.p. 101°C) at a reaction temperature of 90°C and dimethylacetamide (b.p. 165°C) at a reaction temperature of 100°C. In both cases substantial solvent evaporation occurred well before completion of the reaction. The vigorous mixing action of ultrasound especially encouraged vaporisation.

The final choice of solvent was butyl benzoate which has a boiling point of 249°C. Ultrasonic and thermal reactions were carried out at 150°C using 1,6-hexanediol and dibutyltin dilaurate and a 1:1 monomer : solvent ratio. The ratio of δ-valerolactone to initiator was 30:1 and the ultrasound intensity was 18.4 Wcm^{-2}.

Figure 4.29 illustrates the change in polymer molecular weight with reaction time for the ultrasonic experiment. Results are also given for the equivalent ultrasonic reaction performed without solvent. Figure 4.30 presents polydispersity data.

The solution experiment carried out using heat alone gave rise initially to GPC samples with a large amount of low molecular weight material. A clear polymer peak was only detected at 180 min and had an M_n of 5530. The molecular weights of the final two samples were 5580 and 5530.

Figure 4.29

Change in Number Average Molecular Weight with Time for the Ultrasonic Polymerisation of δ-Valerolactone in Butyl Benzoate

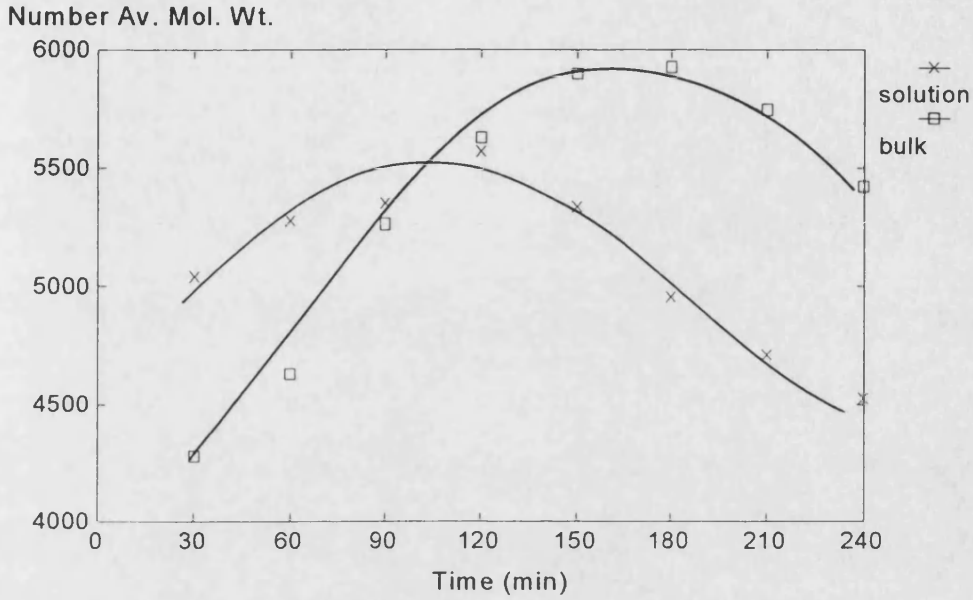
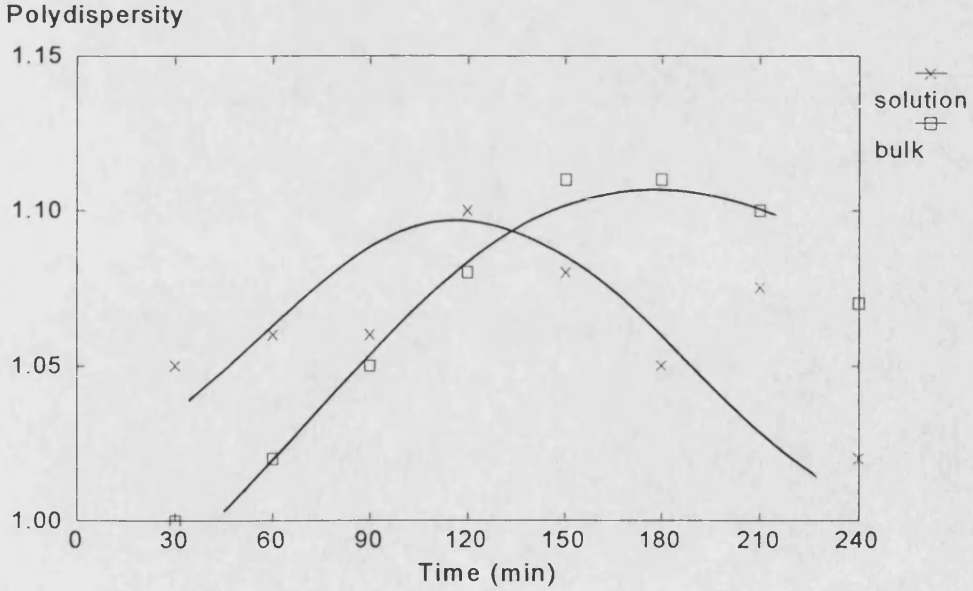


Figure 4.30

Change in Polydispersity with Time for the Ultrasonic Polymerisation of δ-Valerolactone in Butyl Benzoate



Discussion

Figure 4.29 illustrates that, as observed in bulk experiments, polymer degradation occurred when ultrasound was used. No such effect was apparent in thermal reactions. Examination of the bulk and solution curves shows that degradation was more pronounced in the solution experiment, outweighing polymerisation at an early stage in the reaction and resulting in a lower value of maximum molecular weight being obtained.

Other workers have suggested a number of roles that solvent molecules may play in the ultrasonic degradation process. Gooberman[117] explained degradation as being due to the shock wave produced during the collapse of a transient cavity. The shock wave is pictured as a rapid pressure rise, followed by an exponential pressure drop. Alexander and Fox[118] suggested that the number of solvent molecules within the volume enclosed by a macromolecule when the pressure reached its peak, was greater than atmospheric pressure. During the subsequent pressure drop, the entrained solvent molecules would flow out of the macromolecule setting up stresses in the chain. These were calculated to be of the right order to cause bond rupture.

Other workers have attempted to quantify the shear forces arising from the rapid movement around pulsating cavitation bubbles. Harrington and Zimm[119] degraded polystyrene in a range of solvents and calculated that the forces generated in good solvents (i.e. where polymer chains were stretched) were 3.5×10^{-11} N compared with 4.0×10^{-12} N in poor solvents.

The studies outlined however, concentrated on the degradation of polymers of a much higher molecular weight than the polylactones in the current work (often many

tens of thousands). Features typical of ultrasonic solution degradation (e.g. centre cleavage of molecules and the reaching of a limiting molecular weight) were not observed. As discussed in Section 4.3, the most likely explanation for ultrasonic degradation of polylactones is enhancement of a thermal-type degradation process and this seems to be equally true for bulk and solution experiments. It is therefore necessary to consider further the role that the solvent plays in ultrasonic reactions.

The ease with which cavitation bubbles are formed is highly dependent on the viscosity and density of the liquid undergoing sonication. In a solution of low viscosity and density, it is far easier for molecules to be "pulled apart" to create cavities. Reaction mixtures in bulk lactone experiments (comprising monomer and 1,6-hexanediol) were fairly viscous, but butyl benzoate (the solvent in solution experiments) had a density and viscosity comparable to water. A greater number of cavitation bubbles would therefore have been formed in butyl benzoate and subsequent ultrasonic effects (mixing, heating, bubble collapse etc.) would have been stronger. This is likely to explain the faster polylactone degradation seen in solution experiments over those performed in bulk.

4.7 Ultrasonic Copolymerisation of δ-Valerolactone and ε-Caprolactone

As shown in previous sections, ultrasonically produced polyvalerolactone is prone to degradation during formation, whilst polycaprolactone is relatively stable.

The formation of copolymers of δ-valerolactone and ε-caprolactone both thermally and with ultrasound, enables investigation of a number of factors, including the extent to which the monomers are incorporated into the copolymer for the two

experimental methods and the degree to which ε-caprolactone stabilises δ-valerolactone polymers.

Some conventional copolymerisation studies of δ-valerolactone and ε-caprolactone have been performed previously. Pitt *et al.* [120] produced hydroxy-terminated copolymers using a 1:1 feed ratio of the monomers. They were subsequently reacted with multifunctional isocyanates to generate cross-linked networks. Storey[82] performed experiments using a variety of feed ratios and investigated the melting points and molar composition of the resultant copolymers. Water (rather than a diol) was used as an initiator in work by Yoshida.[121] Copolymers were characterised using GPC, DSC and ^{1}H NMR.

4.7.1 Molecular Weight Trends in Copolymers

In this study, three different copolymer feed ratios were investigated:

Mol % δ-valerolactone	Mol % ε-caprolactone
27.5	72.5
53.3	46.7
77.4	22.6

δ-valerolactone and ε-caprolactone homopolymers had been produced previously (Sections 4.3 and 4.4). Reactions were performed using a 30:1 monomer to 1,6-hexanediol ratio and were catalysed with dibutyltin dilaurate. The reaction temperature

was 150°C and an ultrasonic intensity of 18.4 Wcm^{-2} was used in sonication experiments.

Figures 4.31-4.33 illustrate molecular weight data for the three different feed ratios. Both ultrasonic and thermal results are given Figures 4.34-4.36 are the equivalent polydispersity plots.

The graphs show that the ultrasonic experiments had a faster reaction rate than thermal reactions and gave rise to higher molecular weight polymer with a broader polydispersity. As would have been expected from the reactions already performed, (Sections 4.3 and 4.4), the greater the percentage of ε-caprolactone in the copolymer, the higher the molecular weight.

Degradation was not apparent in the two polymers formed from the 72.5% and 46.7% ε-caprolactone feed: the molecular weight appeared simply to reach a maximum and level off (presumably as determined by the lactone:initiator ratio). The final point on the graph of the polymer containing 77.4% δ-valerolactone showed a fall in molecular weight however, suggesting that degradation was starting to occur. This reinforces the previous ultrasonic work carried out, where δ-valerolactone was found to degrade readily. When a substantial amount of ε-caprolactone was present, the monomer was able to stabilise the polymer and hence degradation was not observed.

Figures 4.37 and 4.38 combine molecular weight results from thermal and ultrasonic experiments for the 5 different compositions studied (3 copolymers and 2 homopolymers).

The graph from thermally produced samples, (Figure 4.38), shows that the molecular weights obtained for the three copolymers fell within a relatively narrow

Figure 4.31

Change in Number Average Molecular Weight with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 27.5 : 72.5

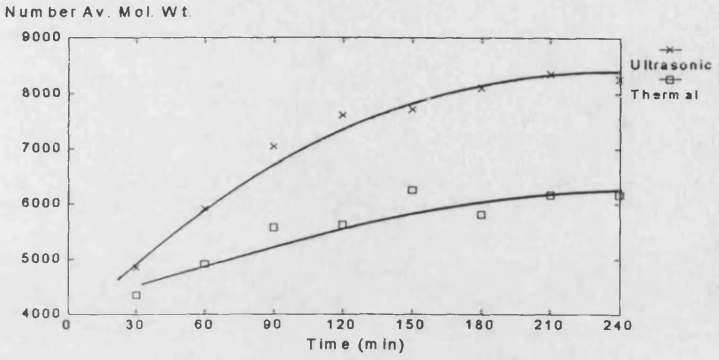


Figure 4.32

Change in Number Average Molecular Weight with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 53.3 : 46.7

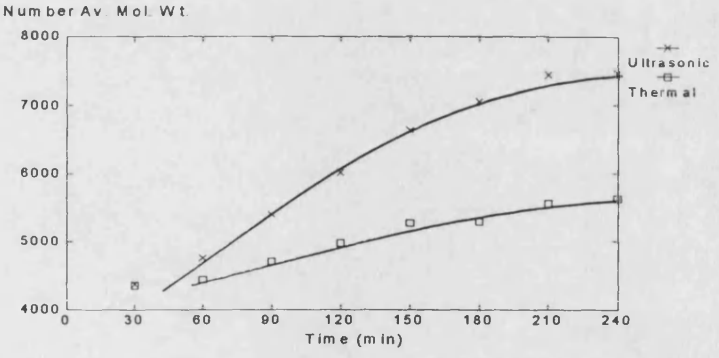


Figure 4.33

Change in Number Average Molecular Weight with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 77.4 : 22.6

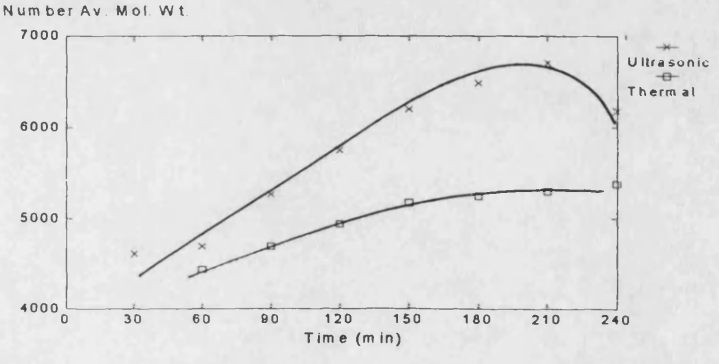


Figure 4.34

Change in Polydispersity with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 27.5 : 72.5

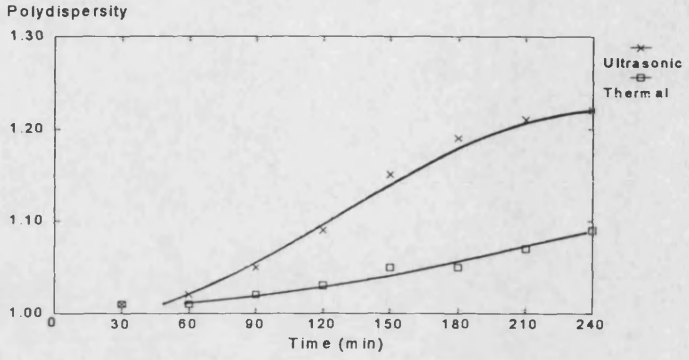


Figure 4.35

Change in Polydispersity with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 53.3 : 46.7

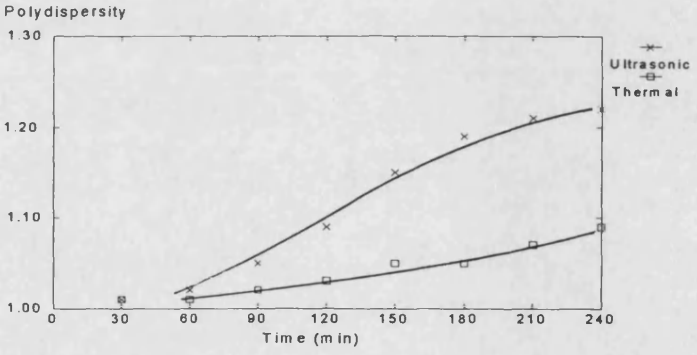


Figure 4.36

Change in Polydispersity with Time for the Ultrasonic and Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone: Feed Ratio 77.4 : 22.6

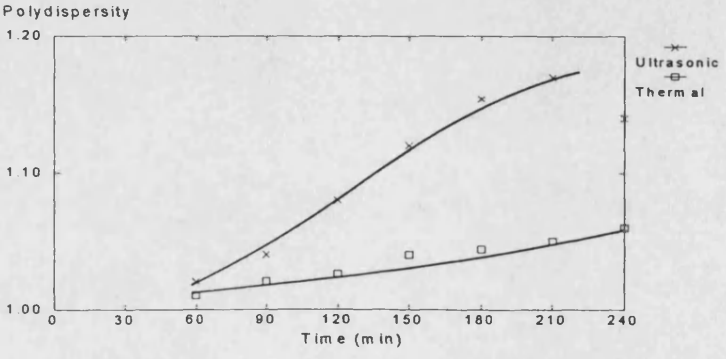


Figure 4.37

Change in Number Average Molecular Weight with Time for the Ultrasonic Copolymerisation of δ-Valerolactone and ε-Caprolactone for a Range of Feed Ratios

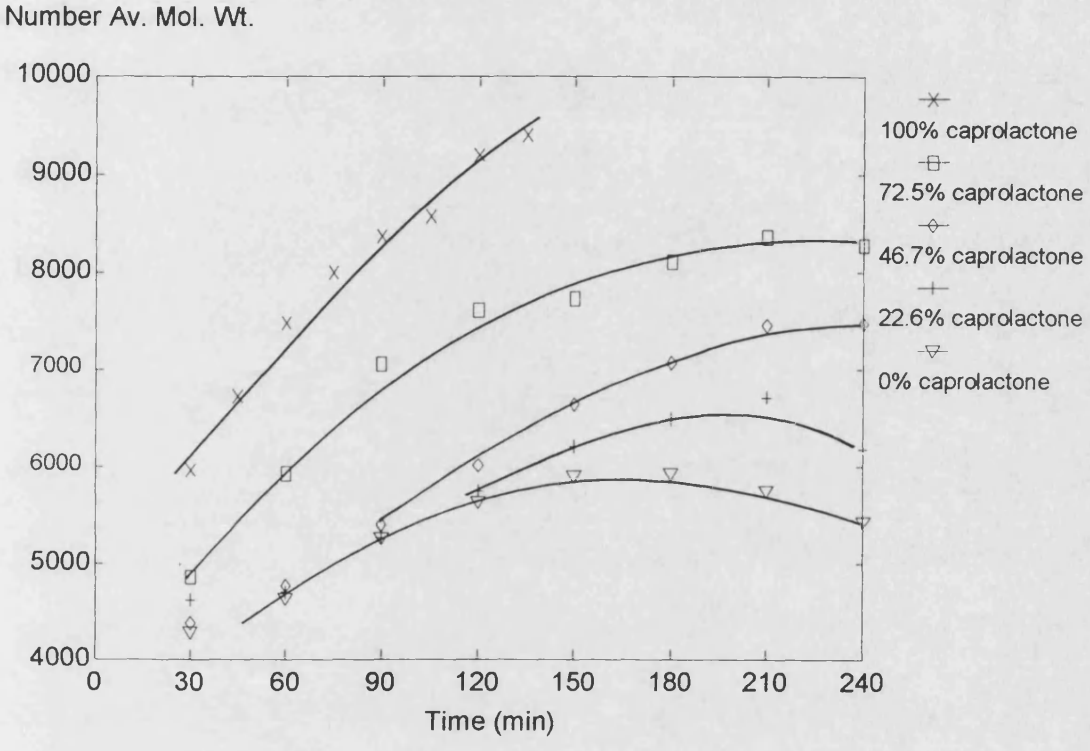
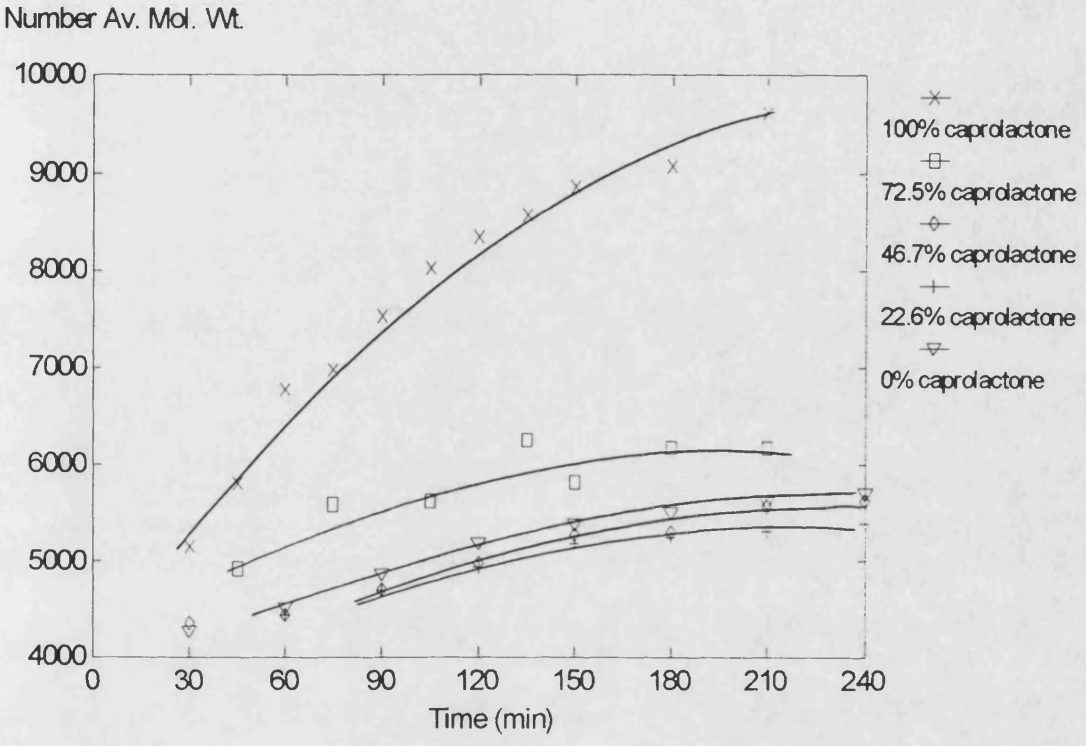


Figure 4.38

Change in Number Average Molecular Weight with Time for the Thermal Copolymerisation of δ-Valerolactone and ε-Caprolactone for a Range of Feed Ratios



band of less than 1000 units i.e. differences between them were not marked. Values did not approach those obtained for the caprolactone homopolymer.

The plot of ultrasonic results, (Figure 4.37), illustrates a far greater spread of copolymer molecular weight values, with better defined differences between each composition. The higher ultrasonic molecular weights over thermally produced material, could indicate a greater incorporation of ε-caprolactone into the copolymer structure than was suggested by the feed ratio. This will be examined in greater detail in Sections 4.7.2 and 4.7.3 (DSC and NMR studies).

4.7.2 Differential Scanning Calorimetry of Copolymers

To determine the melting points of the copolymers and to discover any differences between equivalent thermal and ultrasonic samples, differential scanning calorimetry was carried out.

A typical trace is shown in Figure 4.39. In all cases a melting transition was found and it was generally observed to be sharp, probably due to the relatively low molecular weight and narrow polydispersity of the copolymers.

Figure 4.40 is a plot of melting point against mol % δ-valerolactone in the copolymer feed for both thermal and ultrasonic material. The melting point values for the homopolymers refer to samples produced thermally and are in good agreement with literature values.[121]

The general trend shown by both thermal and ultrasonic copolymers was for a depression in melting point when compared with the homopolymers. This has been observed by several workers. Storey[82] for example, found a minimum melting point

Figure 4.39

DSC Chromatogram for Polycaprolactone

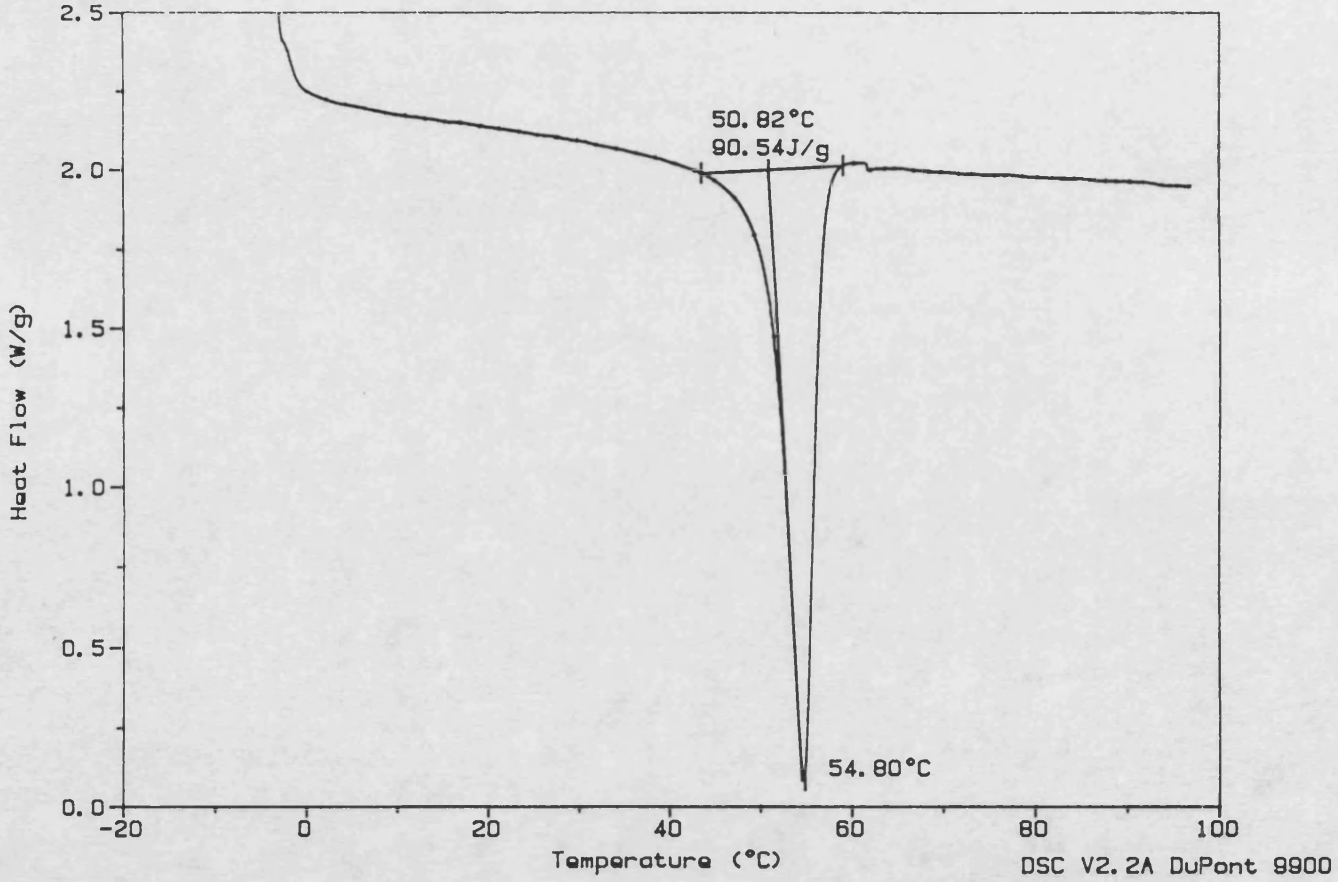
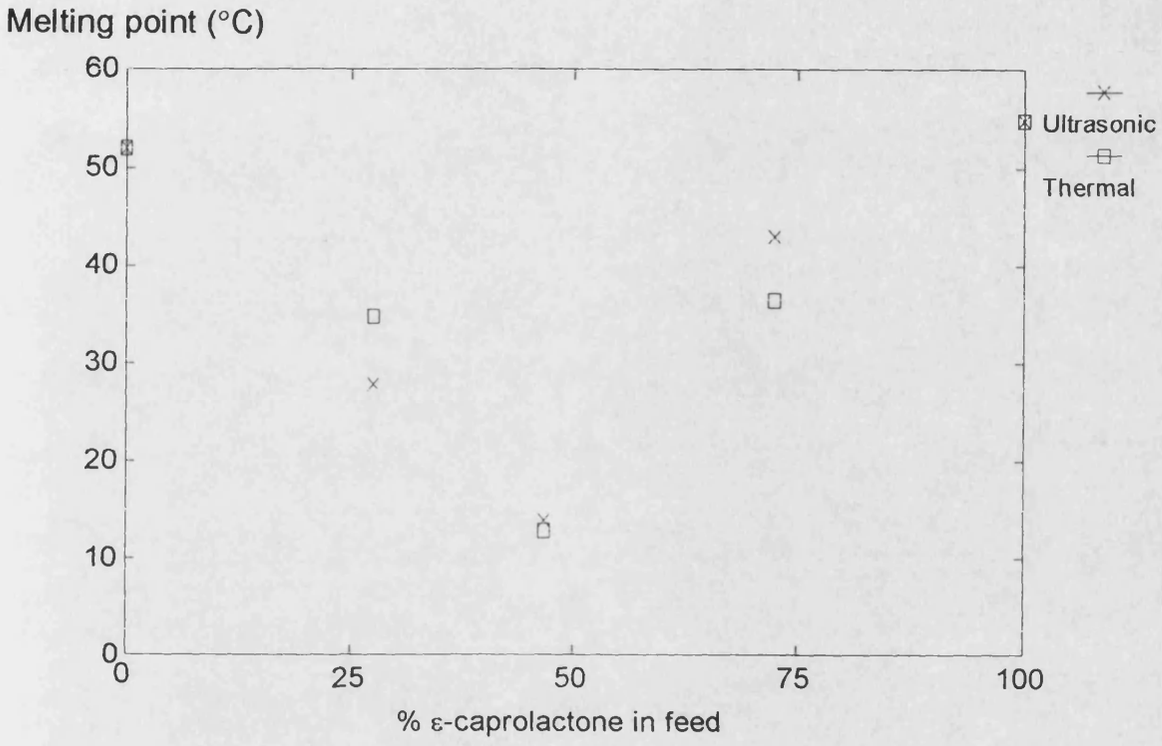


Figure 4.40

Variation of Melting Point with Feed Composition for δ-valerolactone and ε-caprolactone Copolymers



for an approximately 60 mol % ε-caprolactone feed. He also performed a study of the melting points of the blends of the two monomers. No melting point depression was seen in these blends, showing that such a fall is an indicator that true copolymerisation has taken place. Yoshida[121] suggested that the fall was due to a rapid decrease in block lengths of ε-caprolactone and δ-valerolactone units and hence a distortion of crystal structure. He carried out X-ray diffraction measurements on the copolymers to support this.

It is evident from Figure 4.40 that a difference in composition existed between the thermal and ultrasonically produced copolymers. The tendency towards a higher melting point for the ultrasonic materials containing larger amounts of ε-caprolactone in the feed (73 mol %, 47 mol %), suggested that incorporation of ε-caprolactone was greater than the feed level (ε-caprolactone has a higher melting point than δ-valerolactone). In contrast, the ultrasonically produced material containing a large amount of δ-valerolactone (77 mol %), had a lower melting point than the thermal equivalent. This suggested a larger incorporation of δ-valerolactone than would have been expected.

4.7.3 ^{1}H NMR Analysis of Copolymers

It was decided to use ^{1}H NMR to investigate more fully the composition of the δ-valerolactone and ε-caprolactone copolymers.

Figures 4.41 and 4.42 are the ^{1}H NMR spectra for the homopolymers of δ-valerolactone and ε-caprolactone respectively. Peak assignments are given. It can be

Figure 4.41

^{1}H NMR Spectrum of thermally produced Polyvalerolactone

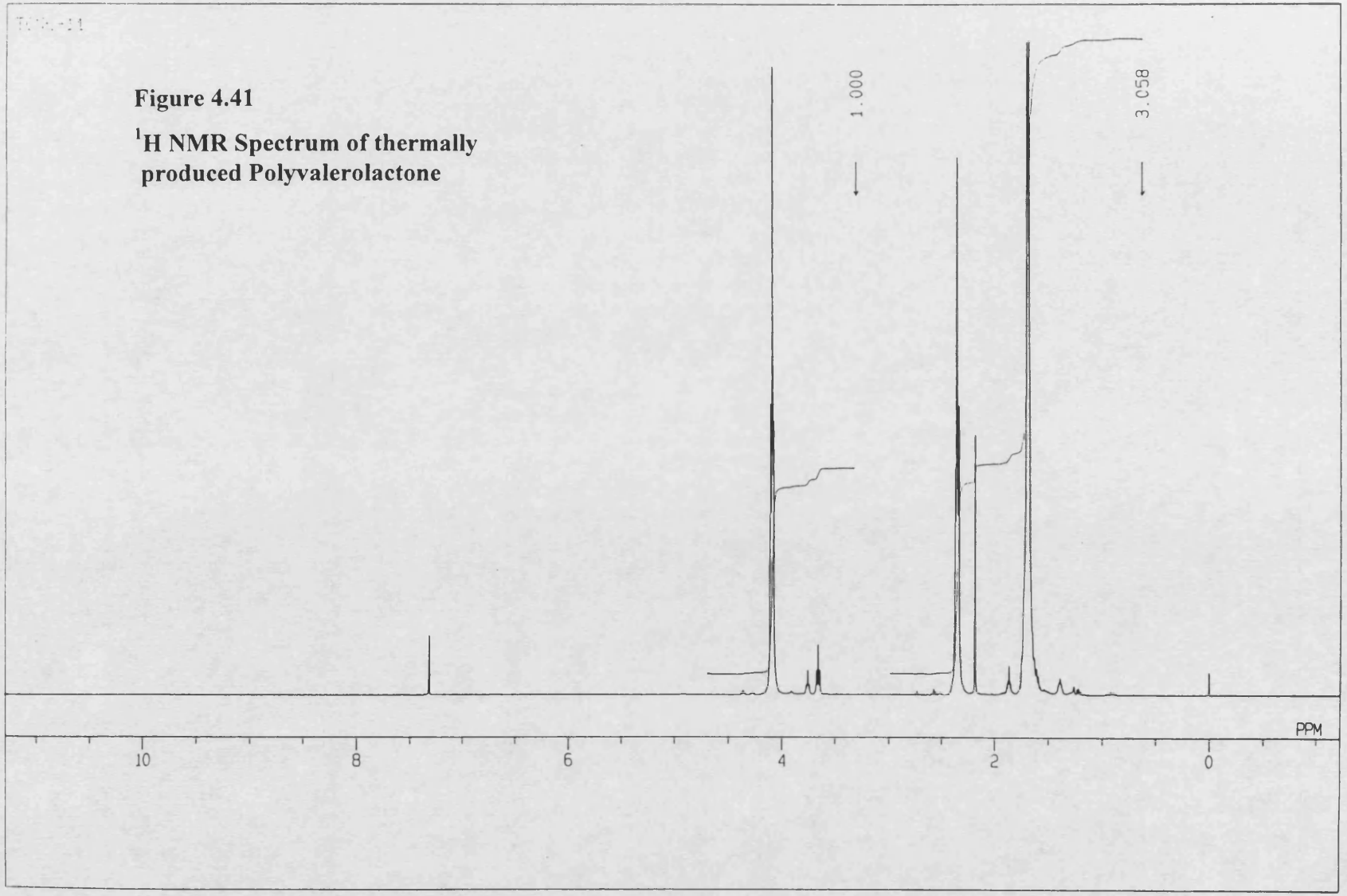
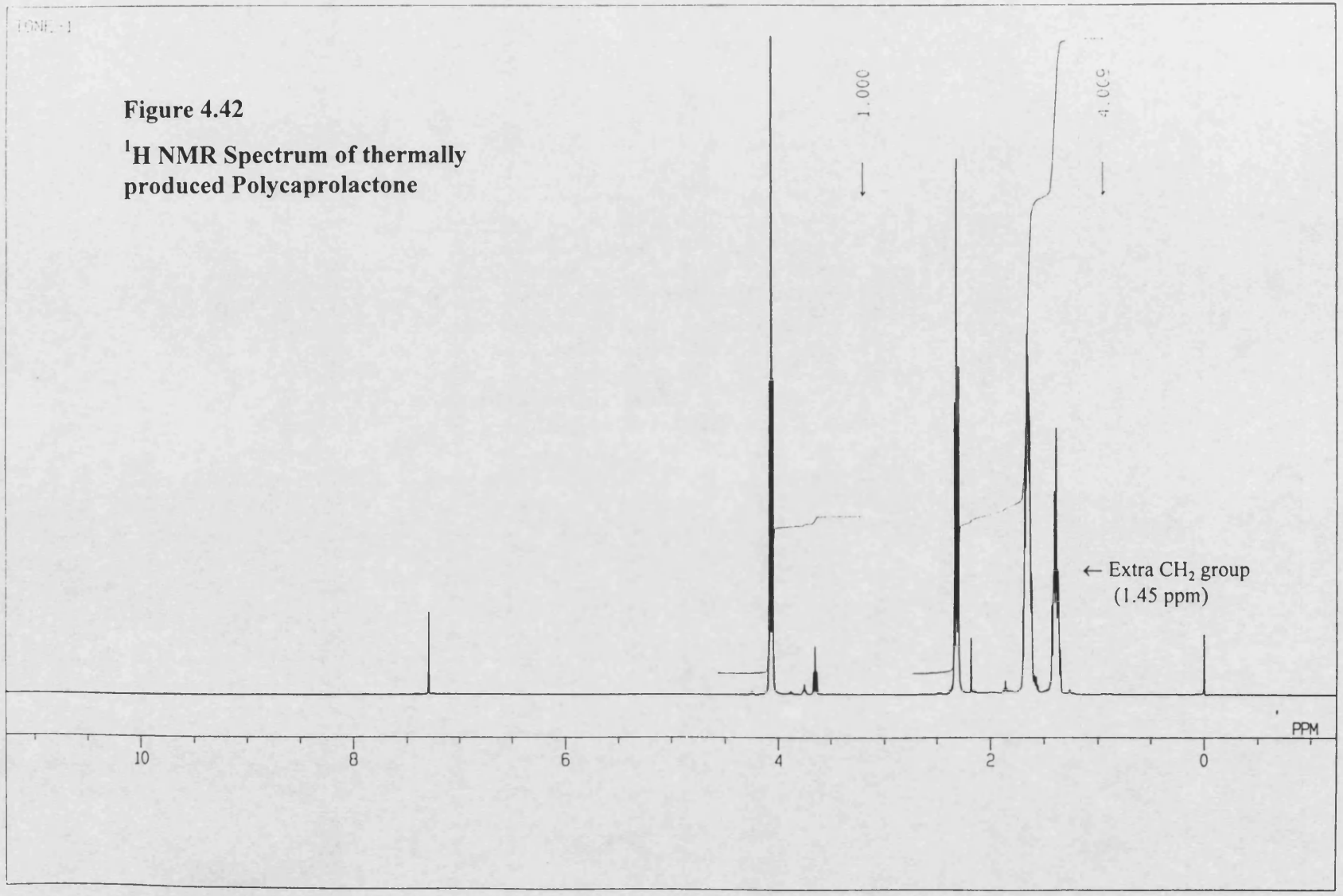


Figure 4.42

^{1}H NMR Spectrum of thermally produced Polycaprolactone



seen that polycaprolactone has an additional peak in its spectrum, (1.45 ppm), corresponding to the extra methylene group in the monomer unit.

Figure 4.43 illustrates the ^{1}H NMR spectrum for the thermally produced copolymer having a 77.4 : 22.6 δ-valerolactone:ε-caprolactone feed ratio. Figure 4.44 is the equivalent ultrasonic spectrum. The ratio of peak integrals present on the spectra confirm the copolymer structure, having values between those for polyvalerolactone (1:3) and polycaprolactone (1:4). The amount of ε-caprolactone in the polymer was determined by considering the 1.45 ppm peak, which as already stated, was due to ε-caprolactone alone. Ratioing the height of this peak to the height of the peak at 4.08 ppm (equivalent to 2H) gave the percentage of ε-caprolactone present.

Expected results (based on the monomer feed ratios) and actual results (from ^{1}H NMR) are given below. Uncertainties in the NMR values (a consequence of integral height measurement) are also listed.

Feed Ratio (mol %)		^{1}H NMR Composition (mol %)		^{1}H NMR Composition (mol %)	
		Thermally produced polymers		Ultrasonically produced polymers	
CL	VL	CL	VL	CL	VL
100	0	100	0	-	-
72.5	27.5	83.0 (± 2.0)	17.0 (± 0.5)	91.0 (± 2.25)	9.0 (± 0.25)
46.7	53.3	60.5 (± 1.5)	39.5 (± 1.0)	68.0 (± 1.75)	32.0 (± 0.75)
22.6	77.4	29.0 (± 0.75)	71.0 (± 1.75)	46.0 (± 1.0)	54.0 (± 1.5)
0	100	0	100	-	-

Figure 4.43

^{1}H NMR Spectrum of an ultrasonically produced δ-Valerolactone-ε-Caprolactone Copolymer, having a Momomer Feed Ratio of 77.4 : 22.6

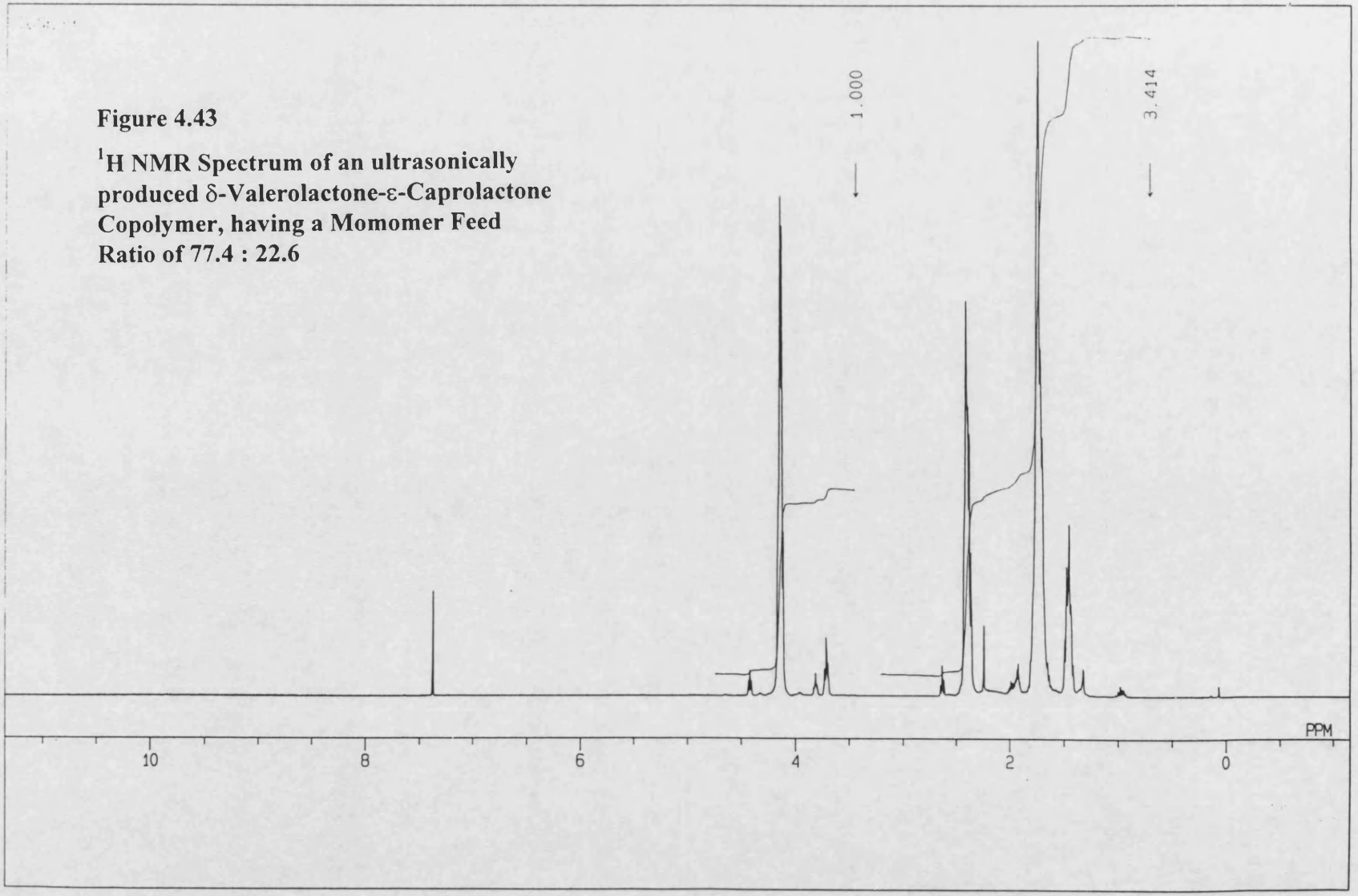
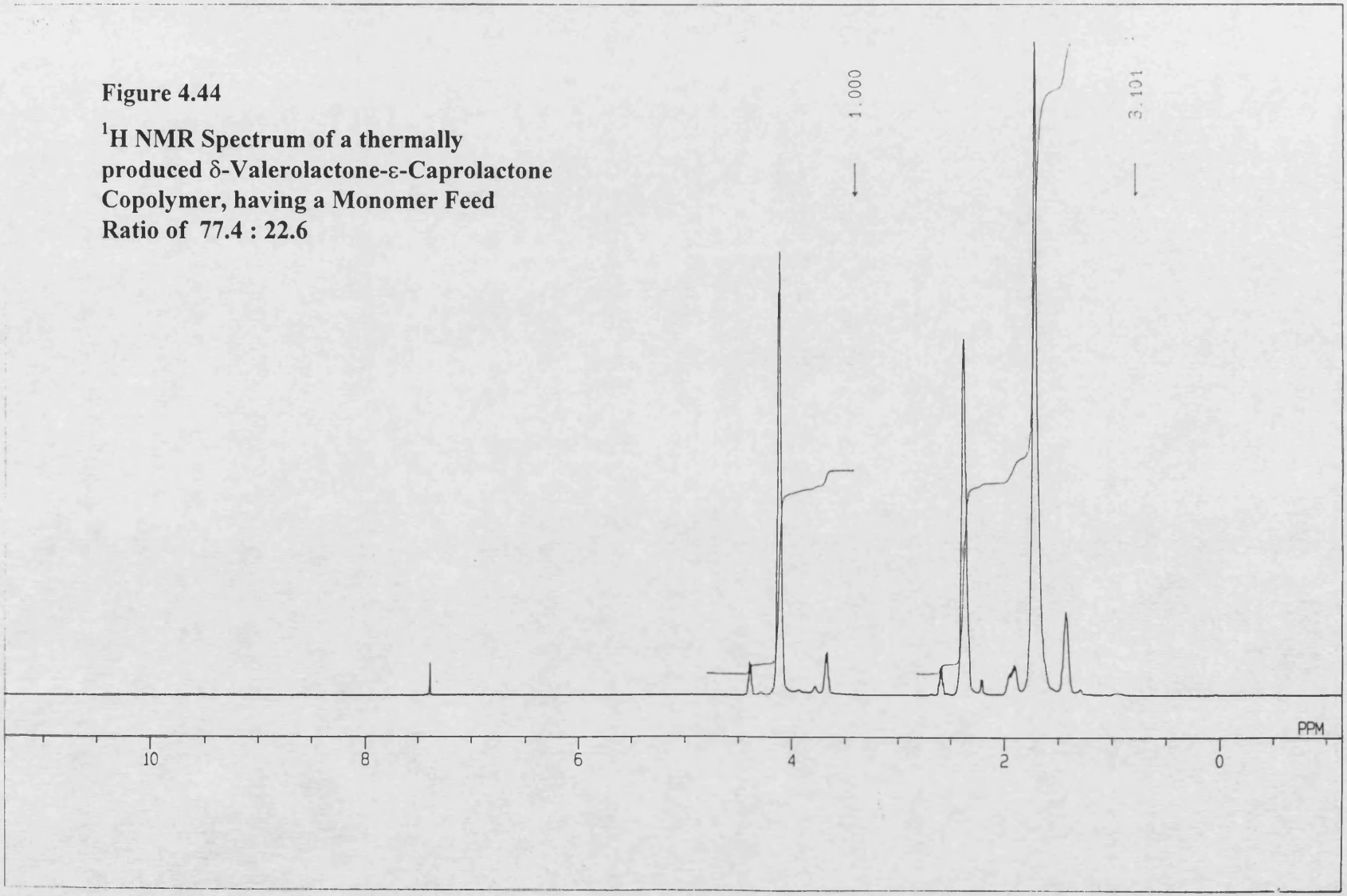


Figure 4.44

^{1}H NMR Spectrum of a thermally produced δ-Valerolactone-ε-Caprolactone Copolymer, having a Monomer Feed Ratio of 77.4 : 22.6



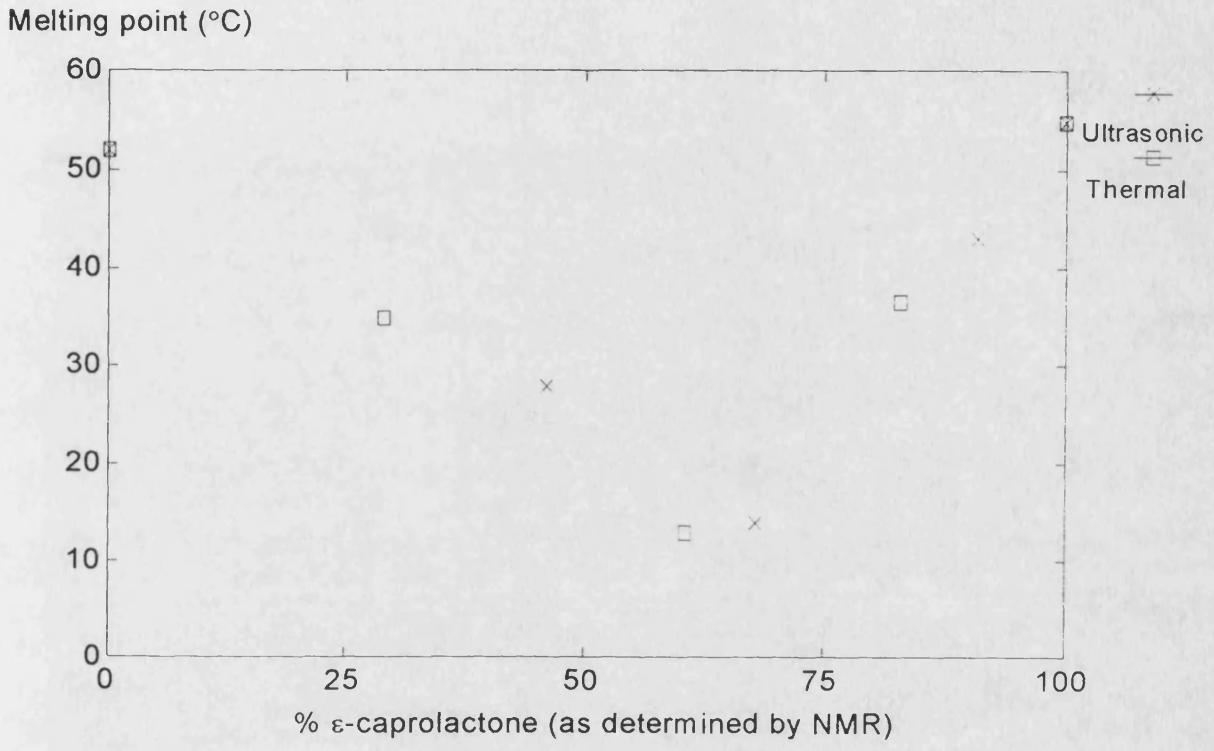
In all cases the percentage of ε-caprolactone on the polymer was higher than in the initial feed, meaning it was preferentially incorporated into the copolymer. Yoshida[91] found similar results when studying the reaction of δ-valerolactone and ε-caprolactone initiated by water at 200°C. Here, ^{1}H NMR revealed ε-caprolactone contents of 92, 78, 71, 53 and 19 mol % for initial ε-caprolactone feeds of 85, 70, 50, 30 and 15 mol %. Yoshida speculated that the low incorporation of δ-valerolactone lay in the varying rates of ring-opening and condensation of the two monomers. Storey[82] also found copolymers richer in ε-caprolactone than expected when carrying out ^{13}C NMR studies. He postulated that at high conversions, depolymerisation of δ-valerolactone became important and this was responsible for the effects seen.

This theory would appear to be in agreement with results seen in the polymers produced ultrasonically in this study. Polymers from ultrasonic reactions had an even higher ε-caprolactone composition than their thermal equivalents. It has already been shown that ultrasound leads to decomposition of polyvalerolactone and this is likely to explain the relatively small proportion of the material in the copolymers.

Now that the actual polymer composition is known, it is possible to re-draw Figure 4.40 (showing DSC melting point results), so that the x axis reflects the true percentage of ε-caprolactone in the copolymer, rather than that in the feed. This is shown in Figure 4.45 overleaf. When experimental error is taken into consideration (± 1°C), it would seem that the values from ultrasonically and thermally produced polymers lie on the same melting point-composition curve i.e. although incorporation of ε-caprolactone is greater in sonicated reaction mixtures, there is no fundamental

Figure 4.45

Variation of Melting Point with Composition (as determined by NMR) for δ-valerolactone and ε-caprolactone Copolymers



difference in the structure and hence melting point between these and thermally produced copolymers.

4.7.4 Discussion of Copolymer Results

As with homopolymerisation, ultrasound was effective at promoting the formation of copolymers at faster rates than conventional heating and stirring. The proportion of δ-valerolactone within the polymer seemed to determine stability, with a large δ-valerolactone composition leading to degradation.

^{1}H NMR measurements revealed that ε-caprolactone was incorporated preferentially into the copolymer, to a greater extent ultrasonically than thermally. Once again it would seem that this is an effect of the relative instability of the δ-valerolactone portions of the polymer and the ability of ultrasound to promote a thermal degradation-type reaction. As discussed by Storey,[82] ε-caprolactone has a larger [M_c] (monomer equilibrium concentration) than δ-valerolactone and therefore its polymerisation is favoured.

The ^{1}H NMR and DSC results were found to be in good agreement, with DSC showing higher than expected melting points for ultrasonic copolymers, indicative of a higher proportion of ε-caprolactone.

4.8 Consideration of Results of Polylactone Experiments

The experiments described in this chapter have revealed a number of important features of ultrasonic lactone ring-opening.

As with the polyurethane reactions studied, ultrasound was found to significantly decrease reaction times and polymerisation was faster at higher ultrasonic intensities.

Of particular interest was the degradation observed in polyvalerolactone experiments. As the molecular weights of the polymers were small, it seemed likely that ultrasound was accelerating a thermal degradation process. No such degradation was seen for polycaprolactone in the time scale of the experiments.

The ultrasonic ring-opening of valerolactone with dibutyltin dilaurate alone gave rise to higher molecular weight polymer without observable degradation. This could have been due to the relatively small number of initiating species giving rise to fewer degradation sites. The equivalent thermal reaction was far less successful. Reaction using only 1,6-hexanediol did not show an increase in molecular weight, giving rise to the theory that the major role of the initiator was to open the lactone ring, whilst the tin salt promoted reaction of the ring-opened monomers.

Solution polymerisation of δ-valerolactone also occurred far more readily using ultrasound rather than heating alone. Degradation was more pronounced than in bulk experiments, suggesting that the decreased viscosity of the solvent gave rise to a greater intensity of ultrasound within the reaction mixture.

Copolymers of δ-valerolactone and ε-caprolactone were formed readily using ultrasound. ^{1}H NMR studies revealed that ultrasonic copolymers contained a significantly greater proportion of ε-caprolactone than their thermal equivalents. This once more illustrated the relative stability of polycaprolactone on exposure to ultrasound.

There are a number of areas which merit further investigation. The design and use of a sealed system for ultrasonic solution work would overcome the problems of solvent loss experienced in this study. It would then be possible to perform experiments using a range of ultrasonic intensities and solvents, to give a better understanding of the process of degradation.

A more extensive copolymer study including a number of feed ratios and in particular a variety of ultrasonic intensities would give more information about the role ultrasound plays in determining composition.

Finally, GPC viscometric analysis of a far larger range of polylactone samples, especially those with a higher molecular weight should lead to the formation of a more accurate relationship between polystyrene equivalent and "true" molecular weight values.

CHAPTER FIVE

CONCLUSIONS

CHAPTER FIVE

Ultrasound has been found to encourage faster polymer formation in both diol/diisocyanate reactions and in the ring-opening of lactones. It also has a significant effect on the molecular weight properties of the resultant polymers, giving higher molecular weight material than conventional (heated/stirred) reactions.

Studies of polylactones revealed that ultrasound promoted a "thermal-type" polymer degradation during the course of ring-opening experiments. A similar molecular weight investigation of ultrasonically produced polyurethanes would be interesting, to discover whether degradation plays a part in other step-growth systems.

The exact method by which ultrasound produces the results observed (whether by heating, stirring or "chemical" effects), is difficult to ascertain. More detailed investigation of reaction kinetics may help to explain the role that ultrasound plays - a thorough study of the mono-alcohol/mono-isocyanate reaction would be a useful starting point. Other possible areas for further investigation have been described in Sections 3.4 and 4.8 and include the use of a sealed cell for polylactone solution work and further lactone copolymer experiments.

In conclusion, current work has shown that despite being little studied to date (previous ultrasonic polymerisation studies having concentrated on free-radical reactions), the application of ultrasound to step-growth processes has great potential in the area of molecular weight control and in initiating polymerisations under mild reaction conditions. The groundwork has been laid for more detailed investigation of both the systems described here and other step-growth polymers (e.g. polyamides,

polyesters) and this should contribute to a greater understanding of the role of ultrasound.

REFERENCES

1. W.T. Richards and A.L. Loomis, *J. Am. Chem. Soc.*, **49**, 3086 (1927)

2. K.S. Suslick, *"Ultrasound: Its Chemical, Physical and Biological Effects"*, V.C.H. Publishers, New York, 1988

3. G.J. Price, "*Current Trends in Sonochemistry*", R.S.C., Cambridge, 1992

4. R.J. Young, *"Introduction to Polymers"*, Chapman and Hall, London, 1991

5. Z. Grubisic, P. Remp and H. Benoit, *J. Polym. Sci., Poly. Lett. Ed.*, **5**, 753 (1967)

6. M.A. Haney, J.E. Armonas, and L. Rosen., *Proc. ACS Div. Polym. Mat. Sci. Eng.*, **54**, 75 (1986)

7. A.P. Cracknell, "*Ultrasonics*", Wykeham Pub. Ltd, 1980

8. T.J. Mason and J.P. Lorimer, "*Sonochemistry*", Ellis Horwood Ltd., Chichester, 1988

9. P. Epstein and M. Plesset, *J. Chem. Phys.*, **18**, 1505 (1950)

10. L.A Crumm, *Nature*, **278**, 148 (1979)

11. H.G. Flynn, "*Physical Acoustics*", Academic Press, New York, 1964

12. W. Lauterborn, *Appl. Sci. Res.*, **38**, 165 (1982)

13. W. Lauterborn and H. J. Bolle, *Fluid Mech.*, **72**, 391 (1975)

14. B.E. Noltingk and E.A. Neppiras, *Proc. Phys. Soc., Ser. B.*, **64**, 1032 (1951)

15. G. Seghal, R.G. Sutherland and R.E. Verrall, *J. Phys. Chem.*, **86**, 2982 (1982)

16. K.S. Suslick, *Science*, **253**, 1397 (1991)

17. M. Margulis, *Adv. Sonochemistry*, **1**, 39 (1990)

18. J.P. Lorimer and T.J. Mason, *Chem. Soc. Rev.*, **16**, 239 (1987)

19. A. Henglein, D. Herberger and M. Guiterrez, *J. Phys. Chem.*, **96**, 1126 (1992)

20. F.R. Young, "*Cavitation*", McGraw Hill, London, 1990

21. G.J. Price and P.F. Smith, *Polymer*, **34**, 4111 (1993)

22. W. Gaertner, *J. Acoust. Soc. Am.*, **26**, 977 (1954)

23. H.J. Eyring, *J. Chem. Phys.*, **4**, 283 (1936)

24. G. Cum, G. Galli, R. Gallo and A. Spadaro, *Ultrasonics*, **30**, 267 (1992)

25. H.H.G. Jellinek, *J. Polym. Sci.*, **22**, 149 (1956)

26. A.W. Brett and H.H.G. Jellinek, *J. Polym. Sci.*, **13**, 441 (1954)

27. H.C. Brown and U.S. Racherla, *J. Org. Chem.*, **51**, 427 (1986)

28. P. Riesz, D. Berdahl, and C.L. Christman, *Environ. Health Perspect.*, **64**, 233 (1985)

29. P.K. Chendke and H.S. Fogler, *J. Phys. Chem.*, **87**, 1362 (1983)

30. K.S. Suslick and D.A. Hammerton, *IEEE Trans. Ultrason. Ferroelec., Freq. Cont.*, **33**, 143 (1986)

31. E.W. Flosdorf and L.A. Chambers, *J. Am. Chem. Soc.*, **55**, 3051 (1933)

32. A.S. Gyorg, *Nature*, **131**, 279 (1933)

33. G.J. Price in "*New Methods of Polymer Synthesis II*", Ed. G. Eastman and J.R. Ebdon, Blackie, Glasgow, in press

34. G.J. Price and P.F. Smith, *Eur. Polym. J.*, **29**, 419 (1993)

35. P.F. Smith, "*Ultrasonically Controlled Preparation of Functionalised Styrene Polymers and Copolymers*", PhD Thesis, University of Bath, 1991

36. H.H.G. Jellinek, *J. Polym Sci.*, **37**, 485 (1959)

37. B.M.E. Van der Hoff and P.A.R. Glynn, *J. Macromol. Sci., Macromol. Chem.*, **A8**, 429 (1974)

38. W.B. Smith and H.W. Temple, *J. Phys. Chem.*, **72**, 4613 (1968)

39. O. Lindstrom and O. Lamm, *J. Phys. Colloid Chem.*, **55**, 1139 (1959)

40. I.E. El'Piner, "*Ultrasound: Physical, Chemical and Biological Effects*", Consultants Bureau, New York, 1964

41. P. Kruus, *Ultrasonics*, **21**, 193 (1985)

42. P. Kruus and T.J. Patraboy, *J. Phys. Chem.*, **89**, 3379 (1985)

43. P. Kruus, J. Lawrie and M.L. O'Neill, *Ultrasonics*, **26**, 352 (1988)

44. G.J. Price, P.F. Smith and P.J. West, *Ultrasonics*, **29**, 166 (1991)

45. G.J. Price, D.J. Norris and P.J. West, *Macromolecules*, **25**, 6447 (1992)

46. S. Watanabe, I. Matsubara, M. Kakimoto and Y. Imai, *Polym. J.*, **25**, 989 (1993)

47. G.B. Long, *United States Patent* 3346472 (1967)

48. V. Ragaini, *Paper presented to 1st European Sonochemical Society Meeting*, Autrans, France (1990)

49. V. Ragaini, *Italian Patent Appl.*, 20478-A/90

50. S.J. Stoessel, *J. App. Polym. Sci.*, **48**, 505 (1993)

51. G.J. Price, E.N.K. Wallace and A.M. Patel, "*Silicone Containing Polymers*", Ed. R.G. Jones, R.S.C., Cambridge, in press

52. G.J. Mennicken, *Oil and Colours Assoc.*, **49**, 639 (1966)

53. C. Hepburn, "*Polyurethane Elastomers*", Elsevier Applied Science, London, 1992

54. J.W. Baker and T.B. Holdsworth, *J. Chem. Soc.*, 713 (1947)

55. G. Allen and J.C. Bevington (Eds.), "*Comprehensive Polymer Science*", Vol. 5, Chap. 22, Pergamon Press, Oxford, 1989

56. A. Farkas and G.A. Mills, *Adv. Catal.*, **13**, 6 (1962)

57. R. Richter and H. Ulrich, "*The Chemistry of Cyanates and their Thio Derivatives*", J. Wiley, New York, 1977

58. S. Wong and K.C. Frisch, *J. Polym. Sci., Poly. Chem. Ed.*, **24**, 2867 (1986)

59. Y. Iwakura, H. Okada and S. Yamashiro, *Makromol. Chem.*, **58**, 237 (1962)

60 S.L. Reegen and K.C. Frisch, *Advan. Urethane Sci. Technol.*, **1**, 1 (1971)

61. P. Krol, B. Atamanczuk and J. Pielichowski, *J. App. Polym. Sci.*, **46**, 2139 (1992)

62. H.G. Wissman, L. Rand and K.C. Frisch, *J. App. Polym. Sci.*, **8**, 2971 (1964)

63. M.E. Bailey, V. Kriss and R.G. Spainburgh, *Ind. Eng. Chem.*, **48**, 794 (1956)

64. W. Hager and K. Ueberreiter, *Makromol. Chem.*, **180**, 939 (1979)

65. C.S. Coughlin and M.Q. Samuels, *Polym. Preprints*, **33**, 1140 (1992)

66. R. Thompson, S.G. Taylor and W.W. McGee, *J. Polym. Sci., Poly. Chem. Ed.*, **28**, 333 (1990)

67. S.D. Bruck, *Biomat. Med. Dev. Artif. Organs*, **5**, 97 (1977)

68. G. Gogolewski, *Colloid Polym. Sci.*, **267**, 757 (1989)

69. R. Patai, "*The Chemistry of Acid Derivatives*", J. Wiley, New York,1979

70. C.A. Bischoff and P. Walden, *Ber.*, **26**, 262 (1893)

71. H. Mark and G.S. Whitby (Eds.), *"Collected Papers of W.H. Carothers"*, Interscience Pub. Inc., New York, 1940

72. S. Sarel and L.A. Pohoryles, *J. Am. Chem. Soc.*, **80**, 4596 (1958)

73. T.L. Gresham, J.E. Jansen and F.W. Shaver, *J. Am. Chem. Soc.*, **70**, 998 (1948)

74. H.F. Mark, N.G. Gaylord and N.M. Birkales (Eds.), "*Encyclopedia of Polymer Science and Technology*", Vol. 11, 98, J. Wiley, New York, 1969

75. H.R. Kricheldorf, R. Dunsing and A. Serra, *Macromol.*, **20**, 2050 (1987)

76. H.K. Hall, *J. Am. Chem. Soc.*, **80**, 6409 (1958)

77. P. Kurcok, J. Penczet, J. Franek and Z. Jedlinski, *Macromol.*, **25**, 2285 (1992)

78. H.R. Kricheldorf, M.V. Sumbel and I. Kreiser-Saunders, *Macromol.*, **24**, 1944 (1991)

79. G. Rafler and J. Dahlman, *Acta Polymer*, **43**, 191 (1992)

80. W.H. Carothers, G.L. Dorough and F.J. van Natta, *J. Am. Chem. Soc.*, **54**, 761 (1932)

81. K. Saotome and Y. Kodaira, *Makromol. Chem*, **82**, 41 (1965)

82. R.F. Storey, K.R. Herring and D.C. Hoffman, *J. Polym. Sci., Poly. Chem. Ed.*, **29**, 1759 (1991)

83. R.D. Lundberg, J.V. Koleske and K.B. Wischmann, *J. Polym. Sci., A-1*, **7**, 2915 (1969)

84. K. Ito, Y. Hashizuka and Y. Yamashita, *Macromol.*, **10**, 821 (1977)

85. P. Dubois, P. Jerome and P. Teyssie, *Makromol. Chem., Macromol. Symp.*, **42**, 103 (1991)

86. A. Schindler, Y.M. Hibionada and C.G. Pitt, *J. Polym. Sci., Poly. Chem. Ed.*, **20**, 319 (1982)

87. K.R. Gorda, D.G. Peifler, R.D. Lundberg and A. Gutierrez, *Polym. Comm*, **32**, 25 (1991)

88. Phillips Petroleum Co., *United States Patent* 3652720 (1972)

89. *United States Patent* 3855357

90. X.D. Feng, C.Y. Song and W.Y. Chen, *J. Polym. Sci., Poly. Lett. Ed.*, **21**, 593 (1983)

91. K. Imasaka, T. Nagai, M. Yoshida, H. Fukuzaki, M. Asano and M. Kumakura, *Eur. Polym. J.*, **26**, 831 (1990)

92. B.P. Chemicals Ltd., "*Determination of Water Content by the Karl Fischer Method*", Method Ref. CQC-0020, (1990)

93. International Isocyanates Institute Inc., "*Recommendations for the Handling of Aromatic Isocyanates*", (1976)

94. American Society for Testing and Materials, "*First Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers*", Test No. D2572 (1991)

95. "*Determination of Total Isocyanate Content of Diisocyanate Materials and Polyurethane Prepolymers*", Smith and Nephew Method No. 33 (1981)

96. *Product Information*: Dicyclohexylmetha-4,4-diisocyanate, Bayer A.G. (1979)

97. *Product Information*: Isophorone Diisocyanate, Hüls

98. A. Weissler, I. Pecht and M. Anbar, *Science*, **150**, 1288 (1965)

99. K.S. Suslick and P.F. Schubert, *J. Am. Chem. Soc.*, **105**, 6042 (1983)

100. P.W. Atkins, "*Physical Chemistry*", Oxford University Press, Oxford, 1986

101. K.G. Flynn and D.R. Nenortas, *J. Org. Chem.*, **28**, 3527 (1963)

102. H.S. Sachdev, S. Thorp and B. Wallace, "*Scan Time*", Spectra Tech. Inc. Newsletter, **23**, 1 (1992)

103. J.W. Baker and J. Gaunt, *J. Chem. Soc.*, **9**, 19 (1949)

104. J. Burkus and C.F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958)

105. S. Ephraim, A.E. Woodward and R.B. Mesrobian, *J. Am. Chem. Soc.*, **80**, 1326 (1958)

106. G. Anzuino, A. Pirro, O. Rossi and L. Polo-Friz, *J. Polym Sci., Poly. Chem. Ed.*, **13**, 1657 (1975)

107. M. Gamiroza-Jukic, Z. Gomzi and H.J. Mencer, *J. App. Polym. Sci.*, **47**, 513 (1993)

108. A.V. Cunliffe, A. Davis, M. Farey and J. Wright, *Polymer*, **26**, 301 (1985)

109. *Health and Safety Data Sheet*, Desmodur Z, Bayer U.K. Ltd., (1983)

110. K. Saotome and Y. Kodaira, *J. Polym. Sci., Poly. Chem. Ed.*, **20**, 319 (1982)

111. A.M. Basedow and K. Ebert, *Adv. Polym. Sci.*, **22**, 83 (1977)

112. G.J. Price, *Adv. in Sonochemistry.*, **1**, 231 (1990)

113. S. Irie and M. Irie, *Radiat. Phy. Chem.*, **40**, 107 (1992)

114. G. Schmid, *Z. Phys. Chem*, **186**, 113 (1940)

115. K. Chen, S. Chen and X. Yu, *33rd IUPAC Int. Symposium on Macromolecules, Conf. Proc.*, (1990)

116. H. Fujiwara and K. Goto, *Polym. Bull.*, **23**, 27 (1990)

117. G. Gooberman, *J. Polym. Sci.*, **42**, 25 (1960)

118. P. Alexander and M. Fox, *J. Polym. Sci.*, **12**, 583 (1954)

119. R.E. Harrington and B.H. Zimm, *J. Phys. Chem.*, **69**, 161 (1965)

120. G.C. Pitt, P. Gu, P. Ingram and R.W. Henderen, *J. Polym. Sci., Poly. Chem. Ed.*, **25**, 955 (1987)

APPENDICES

Appendix 1

Water Content of Hydroxyl Compounds (as measured using the Karl Fischer Method)

Material	% Water w/w (mean of three analyses)
Diethylene glycol	0.14
Triethylene glycol	0.20
Tetraethylene glycol	0.07
PEG 200	0.10
PEG 400	0.13
PEG 600	0.25
1,4-Butanediol	0.40

Appendix 2

Safety Data for Diisocyanates

Material	Hazards	Precautions
H_{12}MDI	Severe irritant of skin and respiratory system. May cause sensitisation dermititis.	Wear rubber gloves, use in fume cupboard.
VM10	Severe irritant of skin and respiratory system.	Wear rubber gloves, use in fume cupboard.
TMXDI	Irritant of skin and respiratory system.	Wear rubber gloves, use in fume cupboard.
IPDI	Harmful, irritant.	Wear rubber gloves, use in fume cupboard.
Desmodur Z	Harmful	Wear rubber gloves.